BAKING SCIENCE AND TECHNOLOGY
in Two Volumes
VOLUME I

A

BAKING SCIENCE

AND TECHNOLOGY

By

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Editor, The Bakers Digest

In collaboration with the staff of the
Siebel Institute of Technology.

In Two Volumes

VOLUME I

Dedicated to

DR. F. P. SIEBEL, SR.

Forceful leader and inspiring teacher

FOREWORD

The Baking Industry, in common with all other food industries, has undergone a revolutionary change during the first half of the Twentieth Century. Benefiting in full measure from the unparalleled progress in science and technology which has marked the past several decades, baking has made use to an increasing extent of scientific principles and methods to increase the artisanship still inherent in the production of baked goods. The time is rapidly approaching when a thorough knowledge of the scientific fundamentals involved in the baking process will become an essential part of every progressive baker's education.

One of the primary aims of the Siebel Institute of Technology over the many decades of its existence has been to promote the scientific advancement of baking. While this objective was attained chiefly through original research and by conducting highly specialized technical training courses, the same goal was also sought by the publication of two editions of the "Siebel's Manual for Bakers and Millers," which for many years represented the outstanding reference work in its field. The last edition of the Manual appeared in 1924, or just prior to the phenomenal advances in biochemistry, physical chemistry, and food technology which are mainly responsible for the more recent improvements in baking practice. Thus, while the Manual served as a useful, and indeed indispensable, companion to the progressive baker of the past few decades, the years have taken their toll and the Manual, in its present form, no longer reflects the current status of baking science and technology.

When it was decided to revise the Manual, an opportunity presented itself to incorporate certain changes in the basic concept of the book. For example, in view of the fact that the modern baker possesses a more extensive basic education than was generally enjoyed by the preceding generation, it was felt that much of the more elementary material included in the Manual could now safely be omitted. It was also deemed desirable to expand the usefulness of the work by the inclusion of an extensive bibliography which will permit the reader, if he so desires, to consult the original sources of information. The bibliography, incidentally, indicates the thoroughness with which the subject matter is covered since it lists in excess of 500 individual references.

It is hoped that this new work will meet with the same favorable acceptance among baking technologists, bakery engineers, production men and baking students as was accorded to the original Manual.

F. P. SIEBEL, JR., *President*
Siebel Institute of Technology

Chicago, Illinois
October 1, 1951.

PREFACE

The purpose of this work is to summarize as precisely as possible the scientific and technological aspects of baking, placing principal emphasis on the production of bread. In this it follows in the footsteps of preceding editions of "Siebel's Manual for Bakers and Millers," which represented pioneering efforts in the dissemination of technical data on baking and milling and for many years served as standard reference volumes in these fields.

The underlying premise of the present work is that once we know *how* and *why* certain reactions occur, we are in a better position to guide their course toward the desired end. To cite but one instance, if we obtain a clear understanding of the nature of yeast behavior and of how it is influenced by any of a series of internal and external factors, we can then control the formulation of a dough and regulate its environmental conditions in such manner that the development of desirable dough characteristics is promoted on the one hand, while that of fermentation irregularities is minimized on the other. An attempt has thus been made to present the basic scientific facts deemed essential to a full grasp of the general subject of baking.

The plan adopted for presenting the subject matter is designed to follow a logical course of development, starting with the purely theoretical considerations of the basic sciences in Part I, progressing in Part II to a more or less detailed description of the various ingredients and materials that find use in baking, and discussing their utilization in actual bread and cake production in Parts III and IV. A final section is devoted to a discussion of the more important types of bakery equipment, noting in particular their more recent improvements.

One of the difficulties faced by an author of a work such as this, which is intended to reach a wide group of readers with a varied educational background, is to arrive at a style of presentation that will not discourage the reader with a limited amount of formal education by being too technical, nor alienate the more advanced reader by being too elementary. Therefore, a special effort has been made to attain a happy medium that will prove satisfactory to both categories of readers. Assuming that the average reader will be one whose formal education ex-

tended through high school, certain portions of the book may seem rather abstruse at first. However, a careful study of Part I should go far in supplying sufficient scientific background information to remove most obstacles to a clear understanding of succeeding chapters.

In the preparation of this work the author has depended considerably upon the researches of innumerable investigators. Whenever possible, he has indicated his debt by literature references to the original studies. He has also been greatly aided by the staff members of the Siebel Institute of Technology, especially by F. P. Siebel, Jr., Kurt Becker, Dr. Joern J. Olshausen, Dwight B. West and Ray Frink, all of whom have been generous with their advice and have reviewed portions of the manuscript. Thanks are also due to Victor E. Marx, Clinton L. Brooke and G. T. Carlin for their interest in reviewing some of the chapters. The discussion of bakery sanitation was supplied by Dr. Edward L. Holmes of the American Institute of Baking.

The author will be grateful for criticisms and suggestions for improvements from readers which could serve him as guides in subsequent revisions of this work.

E. J. P.

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BAKING SCIENCE AND TECHNOLOGY

VOLUME I

PART I—BASIC SCIENCE

CHAPTER I

THE CARBOHYDRATES

Introduction. The carbohydrates constitute one of nature's three great classes of organic compounds, the other two being the fats and the proteins. Essentially, the carbohydrates, no matter what their complexity, are substances which contain only carbon, hydrogen and oxygen. The ratio of the number of hydrogen atoms to oxygen atoms in a carbohydrate molecule is nearly always 2 to 1, as in water. Empirically, therefore, carbohydrates may be considered as "hydrated carbon," as is suggested by their name.

The carbohydrates include a vast number of related products, beginning with simple sugars,* such as glucose (dextrose) and, progressing through double sugars and compound sugars, ending up with the highly complex starches and celluloses. These latter products are basically little more than long chain polymers, consisting of hundreds and even thousands of glucose units, the basic building unit of the carbohydrates. The great range of their properties is due not so much to differences in their composition, but rather to the variations in their molecular structure. Thus it is quite possible for two compounds possessing an identical number of carbon, hydrogen and oxygen atoms, i.e., having the same "empirical formula," to show markedly different properties because the molecular arrangement of these respective atoms differs with the two compounds. These differences are disclosed in the so-called "structural formula" of compounds. As an example, both ethyl alcohol, which is ordinary grain alcohol, and methyl ether have the same empirical formula, C_2H_6O. While these two substances have many properties in common, they also differ markedly in others. These different characteristics are explained on the basis of the different structural arrangement of their molecules as shown in the following structural formulas:

Ethyl Alcohol   Methyl Ether
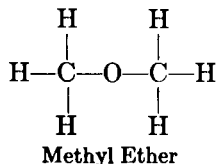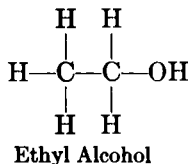
* Actually the simplest hydrate of carbon is the gas formaldehyde (CH_2O). The simplest true member of the sugar series is glycollic aldehyde ($C_2H_4O_2$) which is a sweet crystalline substance readily dissolved in water.

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Substances having the same empirical formula but different molecular arrangements of the atoms are called isomers. While the example given above does not involve carbohydrates, the phenomenon of isomerism is quite common among this group of compounds, as it is in organic compounds generally.

One of the most fundamental reactions occurring in nature—fundamental because it is at the basis of all plant and animal life, including that of man—takes place in the green leaves of plants and is called *photosynthesis*, which means "synthesis with the assistance of light." While this process of combining carbon dioxide and water to form food of high energy value is an extremely complex one, it may be summarized by the following relatively simple equation:

$$6CO_2 + 6H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2$$

This equation may be interpreted as follows: Photosynthesis involves the combination of six molecules of carbon dioxide (CO_2) with six of water (H_2O) through the energy supplied by sunlight to yield one molecule of glucose ($C_6H_{12}O_6$) as the main product and six molecules of oxygen (O_2) as a by-product. It is in this process that glucose, which we have designated as the building stone of all higher carbohydrates, is formed.

The above equation also contributes to an understanding of one of the main attributes of most carbohydrates, namely their high energy value. It will be noted that in this equation energy is designated on the left but not on the right of the arrow. This does not mean, however, that the energy has been lost. It means that the energy has been incorporated into the glucose molecule in the form of chemical energy. When the glucose molecule is again broken down, in a process called *respiration*, it yields up its energy in the form of heat. Ordinary respiration involves the following reaction which, as can be seen, is an exact reversal of photosynthesis:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy$$

Plants always produce more glucose than they immediately require for energy purposes. The excess glucose is transformed by the plant into complex carbohydrates such as starch, which may either enter into the structure of the growing organism or be stored away as a reserve food supply for future use. Cellulose, an important structural component of plant tissue, is another highly complex carbohydrate formed by the union of a great many glucose molecules. Fats, which play some part in the structure of plant bodies, and a greater part in the structure of most animal bodies, are also composed of the same elements as are

carbohydrates, but in different proportions and arrangements. Plants produce fats by transforming carbohydrates so that these substances are also derived from the original glucose. The same holds true of proteins, although in a different sense. Protein molecules are exceedingly large and complex. In addition to hydrogen, carbon and oxygen, they contain always nitrogen, often phosphorus and occasionally sulfur. These elements are obtained by the plant from the soil in the form of inorganic salts. The cells of the plant combine the glucose with nitrogen, sulfur and phosphorus to build up the complex protein molecules.

Glucose, simplest of the sugars, is thus seen to be one of the most important compounds to life. It serves as the primary source of chemical energy, as the basic unit from which all higher carbohydrates and the fats are formed, and it enters importantly into the synthesis of the proteins.

STRUCTURE OF MONOSACCHARIDES

All simple sugars contain hydroxyl groups (OH), and also either an aldehyde group (—CHO or $\overset{|}{\underset{H}{C}}$=O) or a keto group ($\overset{C}{\underset{C}{|}}\overset{|}{C}$=O). Depending on which of these latter groups is present, we speak of an aldehyde sugar, or aldose, and a ketone sugar, or ketose. Two familiar examples of these respective types of sugars are dextrose and levulose, whose structural formulas are as follows:

$$
\begin{array}{cc}
\text{C—HO} & \text{CH}_2\text{OH} \\
| & | \\
\text{H—C—OH} & \text{C}=\text{O} \\
| & | \\
\text{HO—C—H} & \text{HO—C—H} \\
| & | \\
\text{H—C—OH} & \text{H—C—OH} \\
| & | \\
\text{H—C—OH} & \text{H—C—OH} \\
| & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
\text{Dextrose} & \text{Levulose}
\end{array}
$$
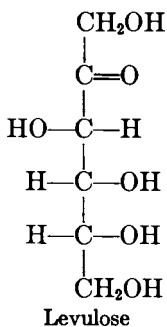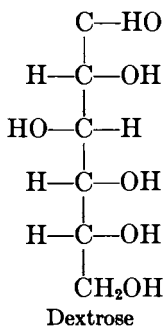
Simple sugars have the general formula $(CH_2O)_n$, although there are some sugars in which the ratio of hydrogen atoms to oxygen atoms is not 2:1, an example of such a deviation from the general rule being rhamnose with a formula $C_6H_{12}O_5$. Monosaccharides vary in the length of their carbon chain and are classified in accordance with the number of the carbon atoms they contain as trioses (3 C atoms), tetroses (4 C

atoms), pentoses (5 C atoms), hexoses (6 C atoms). In the way of example, such natural sugars as arabinose, xylose and ribose are pentoses, and glucose, fructose, mannose and galactose are hexoses.

In visualizing the structural configuration of such a typical hexose as glucose, the carbon chain should be thought of not as straight, but rather as a partly closed chain, as indicated in the following model:
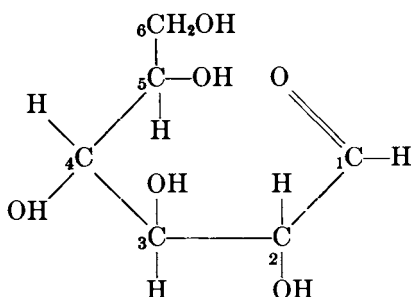
As a matter of fact, when glucose is in solution, a very minute portion of it is found in this form. In nearly all glucose molecules, the chain will have closed entirely to form a so-called pyranose ring, with an oxygen linkage between carbons 1 and 5. Two resulting ring structures are normally formed:

Alpha-glucose   Beta-glucose
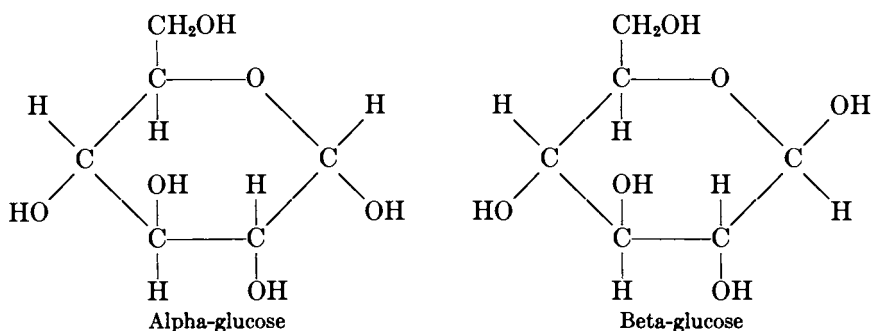
The difference between the alpha and beta forms lies in the relative position of the OH groups on Carbons 1 and 4. In the alpha-glucose the two OH groups are on the same side of the ring, whereas in the beta-glucose they are on opposite sides. When glucose is in solution, about two-thirds of it occurs in the beta-form and one-third in the alpha-form, with only traces in the open chain or aldehyde form. Fructose, a common ketose sugar, possesses analogous ring structures in the alpha and beta-forms:

Alpha-fructose

Beta-fructose
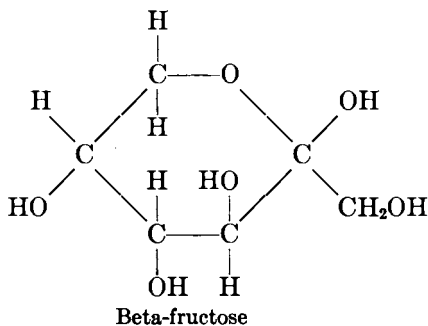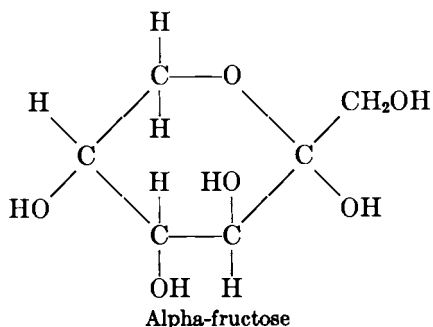
Glucose has the ability to reduce the copper in Fehling's solution (a solution containing certain proportions of copper sulfate, sodium-potassium tartrate and sodium hydroxide) to cuprous oxide. This effect upon Fehling's solution is used to differentiate sugars, such as glucose and fructose, which have a free or potential $-CHO$ group in the molecule from sugars like sucrose which do not. Glucose is called a reducing sugar, whereas sucrose is a nonreducing sugar.

THE DISACCHARIDES

The sugars thus far mentioned have all been simple sugars or monosaccharides, so called because they cannot be hydrolyzed into any sugars of lesser complexity. On the other hand, they form the units from which disaccharides and trisaccharides, or more complex sugars, and eventually the highly complex polysaccharides, such as starch and cellulose, are built up.

Sucrose. By far the most important disaccharide is sucrose, also referred to as cane sugar, beet sugar, saccharose, or simply sugar. It is formed by the union of a glucose molecule and a fructose molecule, with the elimination of one molecule of water, a reaction which may be expressed by the following simplified equation:

$$C_6H_{12}O_6 + C_6H_{12}O_6 \rightleftharpoons C_{12}H_{22}O_{11} + H_2O$$
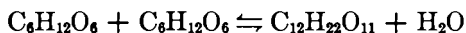
This process is reversible and the complex sugar, with the addition of water, can be made to decompose into its two constituent simple sugars.

In our discussion of the simple sugars only two forms of the ring structure were mentioned, alpha and beta, both of which involve 5 carbon atoms and 1 oxygen atom in the ring. There is, however, a third form, called gamma form, which contains only 4 carbon atoms and 1 oxygen atom in the ring. For fructose, this structure is as follows:
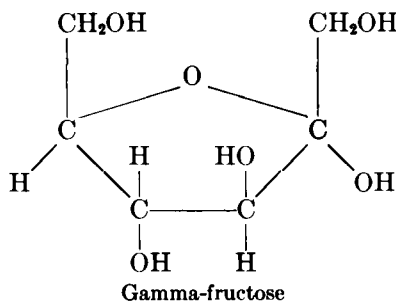
Gamma-fructose

It is such a gamma molecule of fructose which unites with an alpha-glucose molecule to yield a molecule of sucrose which would thus have the following structure:
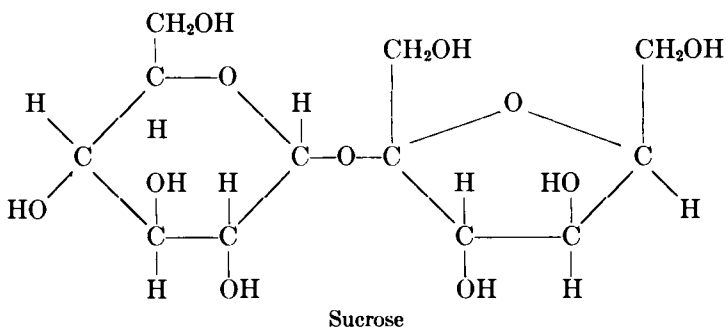
Sucrose

Sucrose is much more stable toward several chemical agents with which the simple sugars react quite readily. It does not reduce Fehling's solution and is therefore a nonreducing sugar. It has a specific rotation of $+66.4°$ (i.e., it rotates the plane of polarized light to the right in a polarimeter). When sucrose is boiled with dilute acids it is hydrolyzed into its constituent sugars, glucose and fructose. This mixture has a specific rotation of $-39°$ (i.e., it rotates the plane of polarized light to the left). The dextro-rotatory sucrose has thus been changed to a levo-rotatory mixture, a process which is called inversion. The mixture itself is known as invert sugar. Inversion may also be brought about by the yeast enzyme invertase.

Maltose. Maltose, a disaccharide, is found principally in malt extract where it is formed by the enzyme activity on starch during germination of the original grain. It is composed of two molecules of glucose with the elimination of one molecule of water, and has the following structure assigned to it:

$_6CH_2OH$
$_5C$——O
H H H
C_4
OH H C——O——C
HO ^{1} ^{4}
C_3——C_2
H OH
Alpha-glucose

$_6CH_2OH$
$_5C$——O
H H OH
C
OH H ^{1}
H
C_3——C_2
H OH
Beta-glucose
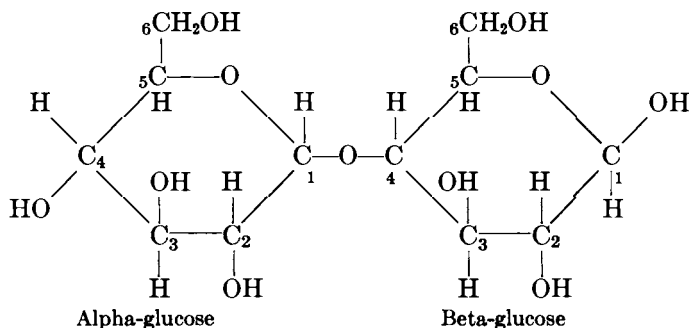
The linkage between the glucose units occurs at the carbons 1 and 4, respectively. It is termed the 1-4 α-glucosidic linkage and is the typical form of union between the glucose units of a starch molecular chain which consists of a long series of alpha-glucose units. This is the type of linkage preferentially split by the enzyme amylase in the conversion of starch to maltose.

There is considerable evidence that there exists an additional linkage in starch which involves the carbons 1 and 6 of the joined glucose units. This is the 1-6 α-glucosidic linkage. Structurally this linkage may be represented as follows:

$_6CH_2OH$
C——O
^{5} H
C C_1
$_4$
C——C O
$_3$ $_2$ $_6CH_2$
$_5C$——O
OH
C_4 C
^{1}
H
C_3——C_2
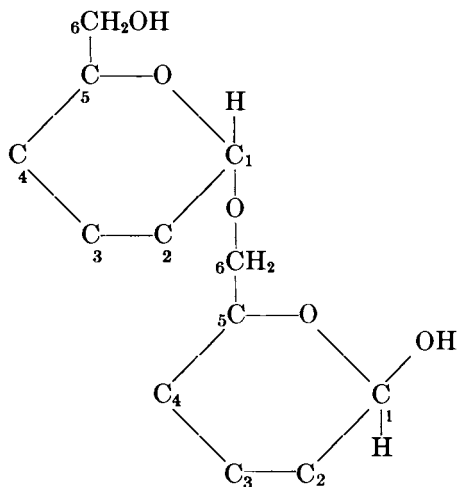
This type of linkage is thought to occur at the point at which the branches of the amylopectin molecules are joined together. This 1-6 α-glucosidic linkage resists the attack of beta-amylase.

The maltose molecule, by retaining a potential $-CHO$ group (on Car-

bon 1 of the end beta-glucose unit) also retains its reducing power and other chemical characteristics that are typical of the simple sugars.

Lactose. Lactose is the principal sugar in the milk of mammals. It is built up from an alpha-glucose molecule and a beta-galactose molecule and resembles maltose in its structural and general properties, being also a reducing sugar. The enzyme lactase is able to hydrolyze it to glucose and galactose. In souring milk it is converted by certain microorganisms into lactic acid $(C_3H_6O_3)$ which is responsible for the characteristic taste and odor of soured milk.

OPTICAL ROTATION

Many substances, including the sugars, possess the property of rotating the plane of light which has first passed through a crystal combination of transparent calcite. The amount of rotation or twisting brought about by an optically active substance can be measured with an instrument called a polarimeter and represents an important specific characteristic useful in determining the nature of the substance thus examined.

The polarimeter is equipped with two prisms of clear calcite, called Nicol prisms, which are mounted at two ends of a closed tube. Calcite, when placed in the path of a light beam, will cut out all vibrations except those in one plane. The light passing through the crystal is called plane polarized light and the crystal itself a polarizer. The second prism, called the analyzer, is so mounted that it can be rotated to both left and right and the degree of rotation measured on a scale. These two prisms at zero position are so aligned that the plane polarized light will pass through the analyzer prism and is visible through the eyepiece. If now a solution of an optically active substance, such as sugar, is inserted between the two prisms in a tube, the light will be partly blotted out. Then on rotating the analyzer, some point is reached when the light is again visible through the eyepiece. The amount of rotation required is indicated on a scale from which the degree of rotation may be read.

Each sugar rotates polarized light through a certain number of degrees, as well as in a certain direction, that is, right (dextro-rotation, $+$) or left (levorotation, $-$). Measurements are usually carried out on a solution containing 1 g. of substance for each ml. of liquid held in a column 10 cm. long, usually with the yellow sodium flame (D-line of spectrum) and at room temperature (20° C.) Under these conditions, the rotation observed with a given substance, and expressed in degrees, is the "specific rotation" of that substance. The specific rotation of glucose is $+52.2°$, and of fructose $-93°$.

When alpha-glucose is dissolved in water, its specific rotation will at first be found to be $+111°$. However, as the solution is left to stand, its

specific rotation decreases to 52.2°. Conversely, beta-glucose in solution will have an initial specific rotation of +19.2°, which gradually increases to a constant 52.2°. This phenomenon of a change in specific rotation is called mutarotation. It is caused by the establishment of an equilibrium between the alpha- and beta-cyclic forms of glucose in solution in which the beta-form predominates. The same type of change is observable in solutions of fructose, with the initial specific rotation of a solution of beta-fructose being −133°.

While the polarimeter is designed for the examination of all optically active substances and can be applied to sugar analysis, a more specialized instrument for use with sugar is the saccharimeter in which the scale used is graduated according to percentage of sugar rather than according to degree of rotation.

THE STARCHES

Starch, the main reserve carbohydrate in the plant kingdom, is also one of its most widely distributed substances. It occurs in seeds and fruits, in tubers and pithy stems, and in leaves, although in the last instance its presence is only transitory. For the purpose of our present discussion, only the starches present in, or obtained from, cereals, tubers and roots are of sufficient interest to warrant detailed consideration. These include the cereal starches, such as those occurring in corn, wheat, rice, etc., and the non-cereal starches finding application to various degrees in baking, such as tapioca starch, potato starch, arrowroot starch, etc. These starches, while similar in their over-all characteristics, differ nevertheless in many essential properties which govern their suitability for certain specialized applications.

When starches from different sources are microscopically examined, they reveal noticeable differences in their physical appearance. Thus the size and shape of the individual granules, the prominence of the granules' hila, and the degree to which striations are discernible, will all be found to vary with starches originating from separate sources. More importantly, such physical properties as swelling, gelatinization temperature, retrogradation, viscosity of pastes, and others, also vary markedly with different types of starches and largely determine their uses for specific purposes. Thus it is the special properties of wheat starches which impart to bread many of its important characteristics. This has been shown by preparing synthetic flours from the protein constituents of wheat flour and starches obtained from non-wheat sources. Such experimental flours fail to bake into satisfactory bread.

Size and Shape of Granules. The size of starch granules, generally expressed in microns (1 μ = 0.001 mm) and signifying the length of their

longest axis, varies from about 2μ to 150μ (*1*). Among the more common types, potato starch granules are among the largest, ranging up to 100μ, while those of rice starch are among the smallest, their range being 3 to 8μ. Granule size within the same type of starch may be either fairly uniform or show quite a spread. Thus potato starch granules may vary in size from 15μ to 100μ, giving a ratio of about 1 to 7, while the range for rice starch granules is from 3 to 6μ, or a ratio of about 1 to 2. Some starches, such as wheat, consist partly of relatively large and partly of relatively very small granules, with few granules of intermediate size.

The average granule size is of some practical significance since it has been found that some starch properties, such as ease of gelatinization or dispersibility, are to some degree correlated with the granule size of a given type of starch. Thus it is a long known fact that the larger granules of any particular starch gelatinize more easily than the smaller granules.

The shape of starch granules, as revealed by microscopic examination, appears to be largely determined by the environmental conditions under which they have grown. For instance, starch granules obtained from a single corn kernel will vary considerably depending on whether they have developed within the glutinous matrix or in the more loosely packed crown of the kernel. The former granules will appear as horny, very angular in shape and highly refractive. Their shape is usually designated as polygonal. The latter granules will appear to be almost perfectly round. Very generally speaking, the horny polygonal granules characterize the cereal starches, such as corn, millet, and rice, while the round, oval and elliptical granules, which usually are also more fragile, are characteristic of tuber and root starches, such as potato, tapioca, sago and arrowroot. An experienced observer can thus usually determine the source of the starch by visual examination under a microscope.

The Hilum and Striations. Some starch granules show a clearly discernible spot, called the hilum. This spot is thought to represent the nucleus around which the granule appears to have grown in some orderly arrangement, suggestive of a crystalline lattice. When observed under a polarizing microscope, the granules light up brightly except for an interference pattern in the form of a "Maltese cross," whose lines intersect at the hilum. This cross effect disappears when an excess of water is taken up by the starch granule, as in gelatinization, indicating that the organizational structure of the granule is weakened or disrupted by the penetrating moisture.

Some starches, notably potato and sago, show pronounced "oyster shell" striations arranged eccentrically around the hilum, while in other starches these seem to be entirely absent. It was formerly thought that

Fig. 1—Tapioca starch under polarizing microscope showing "Maltese cross" pattern.
(*Courtesy Corn Products Refining Co.*)

these striations were indicative of the structural organization of the granule. This view, however, has now been abandoned in favor of another which holds that these markings merely represent the effect of fluctuating growth. Granule development, it is held, does not proceed at an uninterrupted uniform rate, but is subject to fluctuations, resulting in alternately increased and diminished deposition of starch material.
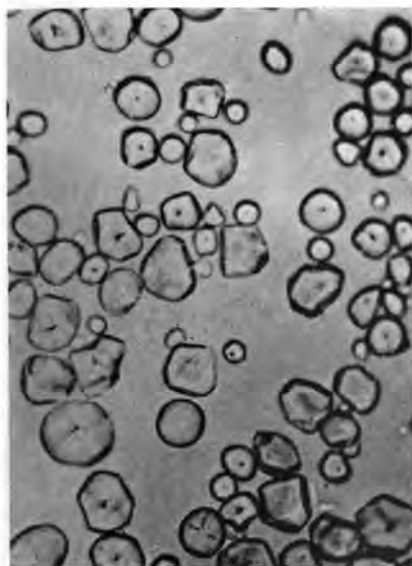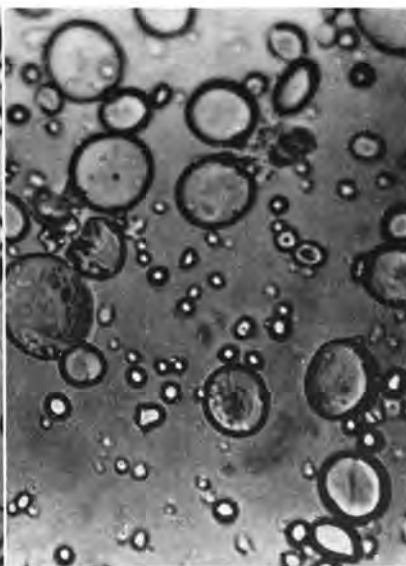
Fig. 2—Corn starch. Fig. 3—Wheat starch.
(*Courtesy Corn Products Refining Co.*)

A brief granule description of the more important starches follows:

Wheat Starch: The wheat starch granules are rather thin and fairly round in form. The hilum, observable in relatively few granules, appears as a dot located eccentrically. Striations are highly indistinct. The starch granules fall into two rather distinct size ranges, the large granules (25μ to 35μ) and the small granules (2μ to 8μ) with practically no intermediate-sized granules. Swollen granules assume a characteristic curved shape.
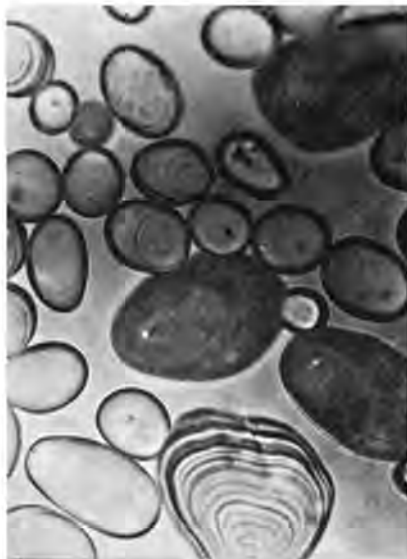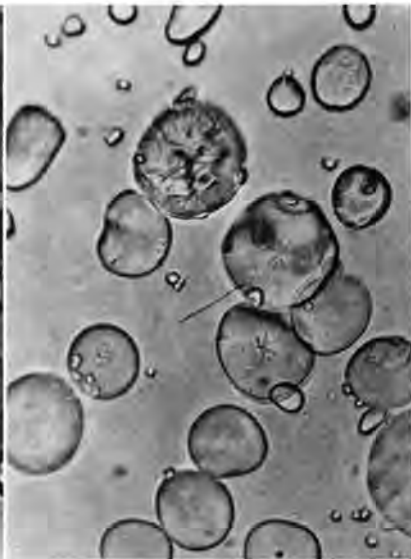
FIG. 4—Potato starch.   FIG. 5—Rye starch.

(*Courtesy Corn Products Refining Co.*)

Corn Starch. Corn starch granules, usually polygonal in shape, except for the round, so-called floury starch, vary in size from 10μ to 25μ. The hilum is quite distinct and starred with fissures. Striation is practically absent.

Potato Starch. The granules of this starch are marked by great variation in size (15μ to 100μ), pronounced "oyster-shell" striations, a flattened ellipsoidal shape, an eccentrically located hilum having the appearance of a black dot, or, at times, of a small split.

Rye Starch. Granules of this starch resemble wheat starch rather closely, except that they are larger and thicker, their average size range approximating 40μ. The granules are further distinguished by very fine striations and the presence of three- and four-fissured hila.

Barley Starch: Granules are either elliptical or round in shape. They show neither a hilum nor distinct striations. Like in wheat starch,

here also two distinct size ranges prevail, 2µ to 6µ, and 20µ to 35µ, except that more of the smaller granules are present than in wheat starch.

Rice Starch: Smallest of cereal starch granules, and also the most generally uniform in size, the distinctly polygonal rice starch granule averages from 3µ to 6µ in size, has no discernible hilum, no visible striations and is translucent.
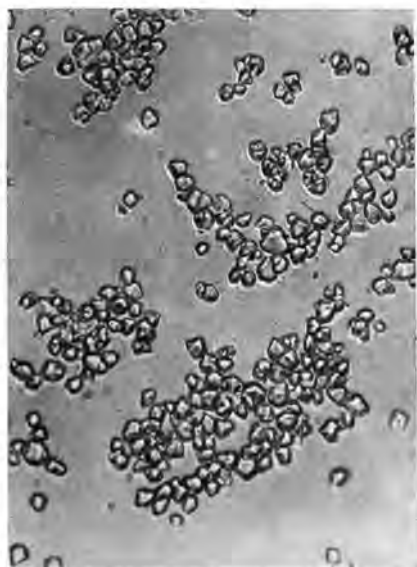
FIG. 6—Rice starch.   FIG. 7—Tapioca starch.
(Courtesy Corn Products Refining Co.)

Tapioca Starch: The granules of tapioca or cassava starch, which average about 20µ in size, are round or oval in shape with a characteristic indentation on one side. The hilum, which is fissured, is centric and striations are absent.

Starch Swelling. The starch granule is completely insoluble in water at room temperature or below. However, when a starch suspension in water is slowly heated, the granules begin to swell rather suddenly when the temperature reaches about 60° C. (140° F.). The granules lose some of their opacity and the Maltese cross effect disappears. With continued application of heat, the granules swell progressively until, at about 85° C. (185° F.), their outlines are no longer discernible. At this temperature, the granules, though extended to more than five times their normal size, are still intact. The great increase in the viscosity of such a heated starch suspension is due to the mechanical jostling of these swollen masses which interferes with the free flow of the water medium. With further

heating, or by vigorous mechanical stirring, the granules finally rupture and disintegrate, giving a colloidal dispersion of greatly reduced viscosity.

Starch swelling may also be observed at room temperature by the use of appropriate salts and alkalis which reduce the specific gel point and are hence called swelling agents. Some of the chemicals which have been used for this purpose, together with their most suitable percentage concentration, are the following: Sodium hydroxide (0.53%), potassium hydroxide (0.75%), potassium iodide (26-28%), ammonium nitrate (30-35%), and silver nitrate (29%). On the other hand, there are other chemicals which tend to increase the gel point. Soaps and vegetable oils are such swelling inhibitors and if, for example, sufficient soap is added to a starch suspension it may be boiled without causing the starch granules to swell appreciably.

The gelatinization phenomenon indicates that, structurally as well as chemically, the starch granule is not a completely homogeneous substance. Thus the outer layer of the starch granule is found to be more dense, less hydrated and less susceptible to enzyme attack than the interior portions of the granule. In its function, this outer layer is suggestive of a sac or envelope enclosing the granule, although this concept cannot be applied too strictly. It will later be seen that there are also some molecular differences which permit the separation of starch into two distinct fractions.

The ease with which amylolytic enzymes convert gelatinized starch into maltose was put to practical advantage during periods of sugar shortage. Thus bakers have found it possible to employ gelatinized starch, supplemented with malted flour or diastatic malt syrup, as a dough ingredient, thereby assuring sufficient sugar production by the action of diastatic enzymes on the convertible starch to maintain a satisfactory level of fermentation after the original flour sugars had been depleted by yeast action, and to provide sufficient residual sugars for the development of a desirable crust color and toasting quality.

Retrogradation. When solutions of starch are held for a prolonged period at room or lower temperature, they undergo a change called "retrogradation." Part of the starch forms aggregates of a micro-crystalline nature and precipitates from the solution. This process may also occur in the solid state, e.g., in bread crumb. The staling of bread appears to be intimately associated with the spontaneous aggregation of the amylopectin or B-fraction of starch, giving rise to a crystalline structure throughout the crumb. The lower the temperature, the more rapid the aggregation or retrogradation, although at temperatures considerably below the freezing point retrogradation is arrested. Retrogradation may also be greatly retarded or entirely prevented if the solution's tempera-
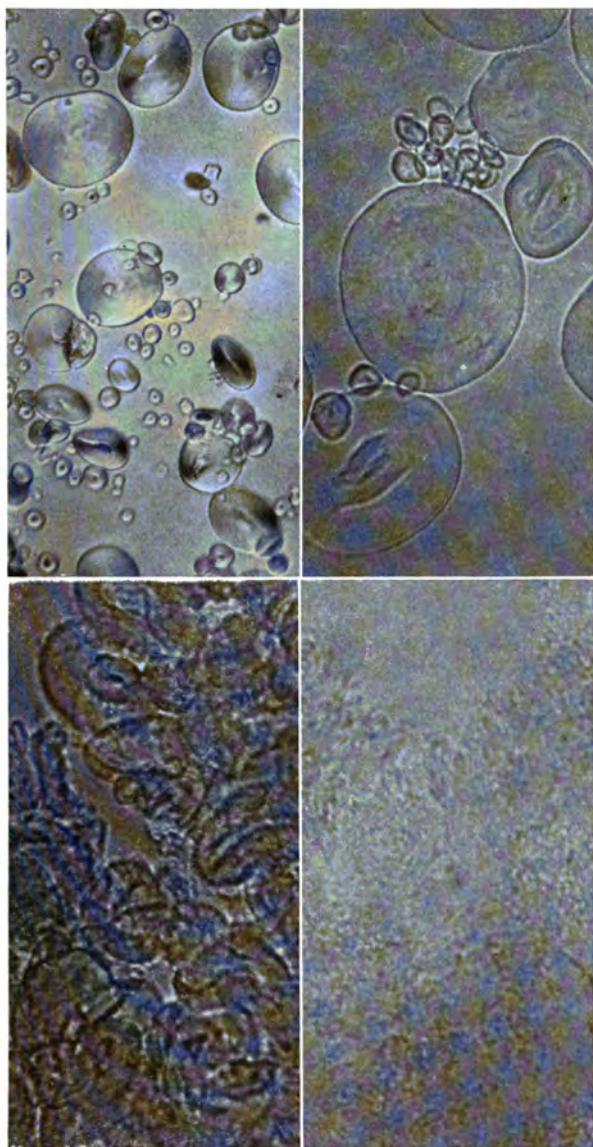
FIG. 8—Gelatinization of wheat starch. (Upper left) mounted in water, not gelatinized; (upper right) gelatinized at 70° C; (lower left) gelatinized at 90° C.; (lower right) gelatinized at 95° C. (*Courtesy University of Illinois Agricultural Experiment Station.*)

ture is maintained at about 55° C. (131° F.). It is also arrested by swelling agents, e.g., alkali and metallic salts, and by reducing the moisture. Thus it is known that crackers do not stale unless their moisture content becomes too high.

Fractionation. Much of past research on starch has concerned itself with its separation into fractions possessing different properties. It has long been known that when swollen starch granules are extracted with hot water, some 5 to 20 percent of the total starch is leached from the granules and can be precipitated by concentration. The starch fraction thus obtained differs markedly in several respects from the remaining swollen granules. More recently, highly exact methods for separating these two components have been developed, yielding fractions of great purity and permitting their closer study.

Starch can be separated into fractions because it consists of two different types of molecules. The component which can be leached from swollen granules is pictured as a long linear chain composed of glucose units hooked together in an uninterrupted series. K. H. Meyer (*2*) has applied the now generally used term "amylose" to this component, which is also referred to as the A-fraction in more recent literature. The starch which remains after leaching consists mainly of highly branched molecules containing several thousand glucose units. This component is termed "amylopectin" or the B-fraction. The difference in the molecular configuration of amylose and amylopectin, i.e., a straight chain as compared to a chain possessing numerous side branches, respectively, explains their behavior during hot water extraction for it would be expected that the amylose molecule would find it much easier to diffuse out of the swollen granule than the amylopectin molecule whose numerous side branches would tend to intertwine with those of neighboring molecules and thereby effectively prevent their diffusion from the granule.

The Starch Fractions. Now that methods for a clear-cut separation of amylose and amylopectin are available, their respective properties can be studied on pure samples. Marked differences in their physical and chemical behavior have been observed. Considering amylose first, it is found that this substance (1) gives a pure deep blue color when treated with iodine; (2) is almost completely converted into maltose when subjected to the action of beta-amylase; (3) has a relatively low molecular weight, corresponding to the presence of from 200 to 300 glucose units; (4) shows an exaggerated tendency to retrograde and to precipitate out of solution on cooling. It possesses several additional distinguishing characteristics, such as high adsorption on cellulose, high degree of crystallizability in certain alcohols, ability to absorb large amounts of iodine in titration, etc. which are of interest primarily to the starch chemist.

A. Dextrose or D-glucose, showing numbering of carbon atoms

B. Maltose, showing α-glucosidic linkage of one glucose unit to carbon atom No. 4 of the other glucose unit

A. Diagram of a fragment of a straight-chain or linear molecule of the amylose fraction of starch.

B. Enlarged view of shaded section of diagram showing chemical structure and linkages.
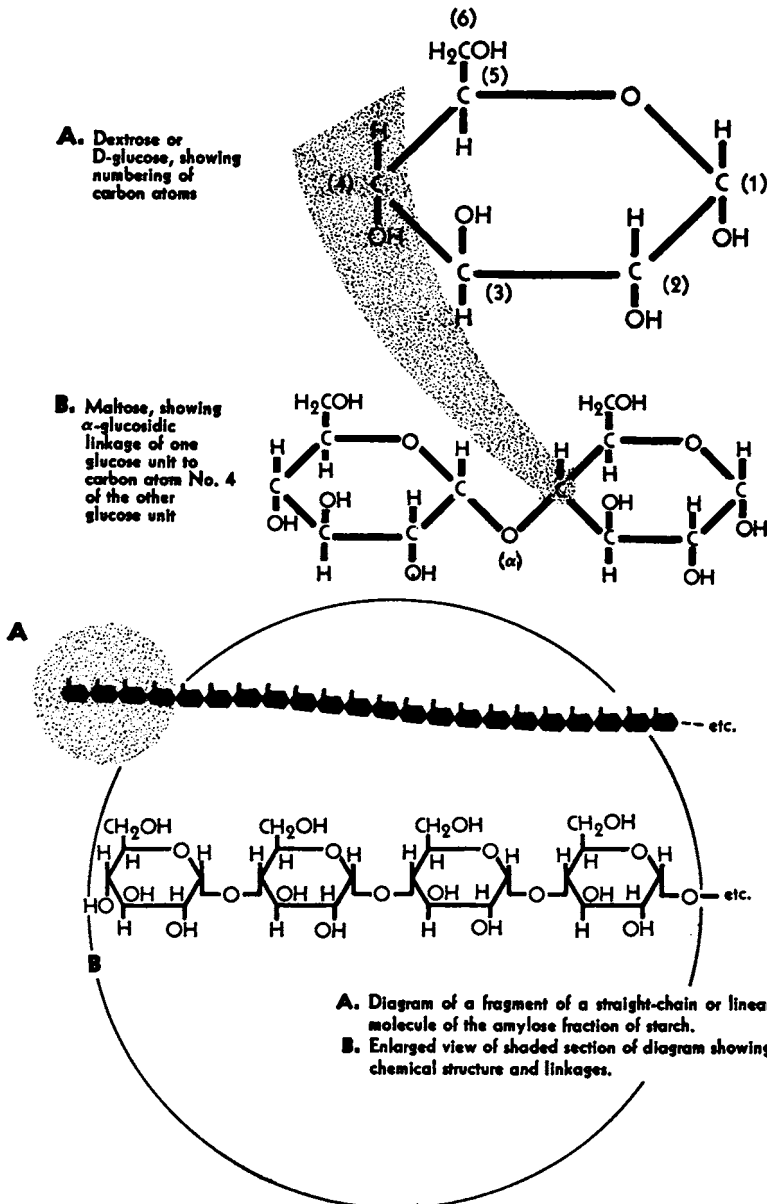
FIG. 9—The linear of glucose chain of amylose (lower part) and the sugars obtained by the hydrolysis of starch (upper part). (*Courtesy U. S. Dept. of Agriculture.*)

The corresponding characteristics of amylopectin are (1) a violet or red-brown color with iodine, (2) limited conversion, up to about 50 percent, on digestion with beta-amylase, (3) high molecular weight indicating the presence of more than a thousand glucose units, (4) low tendency to retrograde.

The distinguishing properties of amylose and amylopectin indicated above conform closely to the respective molecular structures assigned to these fractions. Thus the low solution stability of amylose, i.e., its pronounced tendency to retrograde, may be attributed to the strong associative forces between long linear molecules (*3, 4*). Its complete conversion to maltose by beta-amylase indicates a certain uniformity in the linkages holding the chain together in contrast to the branched amylopectin. Beta-amylase attacks the polyglucosidic chain and splits off two glucose units at a time in the form of a maltose molecule. This reaction goes to completion with amylose. With amylopectin, on the other hand, only about 50 to 60 percent of maltose is produced, the residue consisting of so-called "limit dextrins" or residual dextrins. The explanation for this partial conversion is that enzyme action is arrested at the point of branching in the molecule, as the linkages here are of a type which cannot be split by this enzyme. The limit dextrins represent that part of the molecule from which the side branches extended originally. Various evidence indicates that the amylopectin molecule has some 50 to 70 of these side branches, each averaging 20 to 30 glucose units in length.

While many points relating to the structural configuration of starch molecules are still obscure and debatable, a new and highly promising avenue of approach to the problem has in recent years been opened by the successful synthesis of a starch-like substance in the laboratory. Starch chemists both in this country and in England have been able, through the action of a phosphorylase enzyme on glucose-1-phosphate, to build up a linear glucopyranose polymer which appears to be identical to the amylose fraction of starch. A second phosphorylase enzyme, acting on this synthetic starch, has initiated points of branching, though it appears unable to synthesize high polymeric material. It appears likely, therefore, that the amylopectin fraction is produced in the plant by the action of the two phosphorylase enzyme systems.

Although the amylopectin has a molecular shape which is essentially spherical, in contrast to the linear amylose chain, this does not rule out the possibility that some limited degree of side by side association may take place. Such parallel-wise association of amylopectin branches has in fact been postulated to explain the occurrence of crystalline areas of association, the so-called micelles, within the starch granules. No such micellar association can be observed with glycogen, the animal starch,

A. Diagram of a fragment of a
branched-chain molecule of
the amylopectin fraction
of starch

B. Enlarged view of shaded
section of diagram showing
chemical structure and
linkages at point of
branching
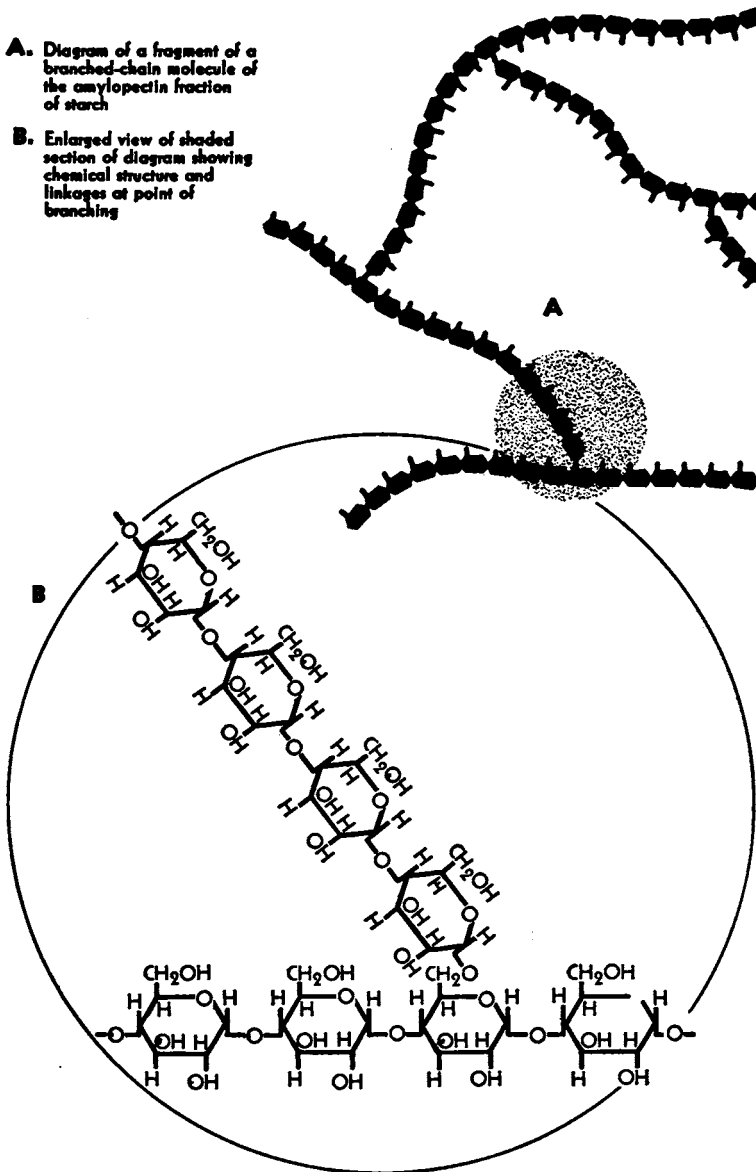
Fig. 10—The branched structure of amylopectin. (*Courtesy U. S. Dept. of Agriculture.*)

which has side chains of only 8 to 10 glucose units in length, nor in limit dextrins in which the side chains have been removed by enzyme action. The staling of bread has more recently been attributed to the gradual and spontaneous aggregation of the amylopectin component of starch. This aggregation may be readily redissolved by the application of moderate heat which is analogous to the refreshening of staled bread.

Occurrence of Fractions. It has been pointed out above that amylose and amylopectin give different color reactions with iodine. A method based on this difference has shown that normal starches, such as corn, wheat, and potato, contain some 21 to 29 percent of amylose, the remainder being amylopectin. Since these starches show considerable differences in the behavior of their pastes, these differences are attributable not so much to the amounts of their respective fractions, but rather to variations within the fractions. Thus the amylose chain of potato starch averages about twice the length of that of corn starch.

FIG. 11—Micellar areas within the starch granule, showing parallelwise association of linear starch chains.

Not all starches, however, conform to the norm. So-called waxy varieties of cereals yield starches composed entirely of amylopectin (5). Such varieties have been discovered in rice, corn, sorghum, rye and barley, but not in wheat, nor are waxy tuber and root starches known as yet. On the other extreme, the starch of the common wrinkled-seeded pea contains some 75 percent of amylose, while that of the smooth-seeded pea is normal in its amylose content. The former starch fails to give a paste in boiling water, the granules retrograding to the insoluble state during the first swelling stage.

Non-Carbohydrate Constituents of Starch. When purified starch is hydrolyzed by a weak acid solution, various non-carbohydrate substances, such as phosphates, lipids, nitrogenous bodies, silica, etc., may be recovered. In all cases this "foreign" material amounts to less than 1 percent of the total starch, characteristic values being approximately 0.46 percent for potato, 0.50 percent for wheat, and 0.74 percent for corn starch. Both the composition and the respective amounts of these non-carbohydrates vary with different starches. Thus in potato and wheat starches the phosphates predominate, in corn and rice starches the fats, etc. Analysis has shown further that these substances are not uniformly

distributed between the two starch fractions. It has been suggested that some of the differences in behavior of the same starch fraction, e.g., amylose isolated from different starches, may be partly attributed to the presence or absence of certain non-carbohydrate substances in them.

Starch Dextrinization. Considering the fact that starch consists principally of glucose units, a surprisingly large variety of breakdown products is obtained when the starch is subjected to the action of different dextrinizing agents.

When starch is exposed to the action of a specific enzyme obtained from the microorganism *Bacillus macerans,* products known as *Schardinger dextrins* are split off. These dextrins consist of short chains containing 6 to 7 glucose units, with their two loose ends united so that the chain forms a ring. These dextrins form beautiful crystals which give a deep blue color with iodine (*5*).

When starch is treated with cold acid for prolonged periods, a partial hydrolysis takes place which dissolves about 50 percent of the starch granules. The insoluble residue, called *amylodextrin,* consists of straight chains approximately 25 glucose units in length and constitutes the crystalline regions in the starch granules which are more resistant to acid hydrolysis than the non-crystalline areas. Amylodextrin closely resembles amylose in its pronounced tendency to retrograde (*6*).

When starch is treated with hot instead of cold acid, the crystalline areas in the granule are destroyed also and the molecules hydrolyzed at random. When hydrolysis is carried to completion, all of the starch is converted into glucose which, when purified, is the familiar dextrose sugar. If hydrolysis is halted prior to complete conversion, a syrup is obtained which contains glucose, maltose, and varying amounts of low-molecular dextrins.

As has already been pointed out, when pure beta-amylase acts on soluble starch, approximately 50 to 60 percent of it is converted into maltose sugar. The remaining portion of the starch has been greatly modified in its properties and has been shown to consist principally of amylopectin molecules whose side branches have been split off by the enzyme. They are termed *limit dextrins* or *residual dextrins.* Their formation is explained on the basis that pure beta-amylase is specific only for a maltose configuration, and that when the enzyme encounters a different configuration its action is arrested. Such different configurations occur in the amylopectin molecule at the points at which the side branches are joined to the main chain. The enzyme beta-amylase occurs in flour in combination with another amylase which can further reduce the limit dextrin.

Dry starch, when heated, is slowly transformed into brown-colored

substances which are soluble in cold water. Their name, pyrodextrins, indicates the manner of their formation. They are thought to be made up principally of the branched-type molecules. The browning of the bread crust during baking, and the coloration of toast, are partly due to the formation of pyrodextrins under the influence of heat.

Enzymatic Modification of Starch. There is a group of enzymes, widely distributed in nature, called diastatic enzymes or amylases, which possesses the ability to split starch molecules into a large variety of conversion products. Only three distinct types of reactions need concern us here: liquefaction, dextrinization and saccharification.

Under normal conditions, it is impractical to assign any of these specific reactions to only one of the two amylases encountered in cereals, namely alpha-amylase and beta-amylase. Thus while beta-amylase is generally termed the saccharifying enzyme because it acts on gelatinized starch to produce the sugar maltose, its action ceases when about 60 percent of the starch is thus converted. However, it also produces dextrins, or complex remnants of starch molecules only partially degraded, and is in this sense also a dextrinogenic enzyme. At the same time, it acts to liquefy the gelatinized starch.

In a similar manner, the alpha-amylase is termed the dextrinogenic enzyme, since it cleaves the long starch molecules into smaller but still complex dextrins. However, it is also a principal liquefying enzyme since it causes gelatinized starch to become solubilized, with a marked reduction in its viscosity and a rapid loss of its iodine color. While very little maltose is initially produced by this enzyme, complete conversion of the starch into maltose is obtained if the action of the alpha-amylase is prolonged sufficiently.

When the action of both of these enzymes is combined, starch conversion to maltose is rapid and almost quantitative. The action is complementary inasmuch as the alpha-amylase splits the starch chains to provide fresh points of attack for the beta-amylase.

Wheat Starch in Baking. While it has long been suspected that the baking quality of different wheat varieties was affected to some degree by varietal differences in their starchy constituents, in addition to the important role played by the protein content and character, relatively little work has been done by cereal chemists until recent years to elucidate this point. A. G. Kuhlman (7) determined the viscosity of gels of different concentrations prepared from starches obtained from wheats possessing varying baking qualities and found that starches from European soft spring wheats of superior baking quality yielded gels having higher viscosities than did starches from soft summer wheats of inferior

baking quality. Furthermore, starches from the better wheats gelatinized upon treatment with a 0.4-0.5 percent caustic soda solution, while starches from the poorer wheats required an alkali concentration of 0.7 percent. Marked differences were also observed between starches from wheats of varying baking quality when their pasting curves were plotted. The same observation as to the differences in viscosities of starch gels prepared from different wheats had previously been made by Alsberg and Rask (*8*) who had found that winter wheat starches gave higher viscosities than did spring wheat starches. However, they also found that significant differences in viscosity existed in gels prepared from samples of the same wheat variety but grown under different environmental conditions.

That the type of wheat should exert an influence upon starch behavior during baking should not be surprising in view of the manner in which the granules are deposited in the endosperm. In so-called hard wheat varieties, the starch is embedded in a rather dense protein matrix with very few "free" granules observable. On the other hand, in soft wheat varieties, with their lower protein contents, more of the granules are in a "free" state. The relative freedom of starch granules in flours would be expected to exert some effect on moisture absorption, though in this they would be overshadowed by the water absorption capacity of the protein constituents, and on the degree of diastatic action. The less protected starch granules would be subject to greater injury during grinding of the wheat and thus be more susceptible to attack by diastatic enzymes (*9*). It is also conceivable that the relative quantities of large and small starch granules present in a wheat variety may have an effect on this. Thus, in a wheat variety having a higher percentage of the larger starch granules, more starch granules would be ruptured during milling than in a wheat having a lower percentage of large granules, so that here again varying degrees of diastatic action would be encountered. Whatever the explanation, the fact that starches from different wheat varieties react differently during the baking process has been well established.

Sandstedt, Jolitz and Blish (*10*) developed a method whereby "synthetic" bread could be produced from gluten and starch previously separated by appropriate washing of a dough and drying. R. H. Harris and L. D. Sibbitt (*11*), utilizing this method, describe experiments in which the baking quality of starches prepared from a series of wheats which included samples of hard red spring, hard red winter, soft red winter, durum, and white wheat classes, was tested by the use of synthetic starch-gluten mixtures. Using a constant gluten substrate ob-

tained from hard red spring wheat, these workers found marked differences in the volume of loaves made from blends employing these different starches. In general, the white-wheat starches yielded loaf volumes which were below the average obtained with red wheat starches. The authors reach the conclusion that "marked differences in those properties that influence baking quality are inherent in starch prepared from different wheat varieties." While it appears that these differences are probably to a large degree heritable, one instance was encountered where considerable disparity of performance occurred between two samples of the same wheat grown in different years, so that a climatic influence is also indicated.

In a subsequent study (*12*), Harris describes in detail the procedures employed and gives the results of further tests. Starches were obtained from five samples of hard red winter wheat and three samples of Siberian wheat grown in Alaska. Samples of corn and potato starch were also prepared in the laboratory and further samples of commercial wheat, corn and rice starch were used. The results obtained when these starches were baked with a constant gluten substrate are shown in the following table:

TABLE 1. BAKING RESULTS COLLECTED FROM STARCH-GLUTEN BLENDS USING A
CONSTANT GLUTEN SUBSTRATE (13.2%) (HARRIS)

Sample	Variety	Wheat Protein %	*Original Flour* Absorption %	Loaf Volume cc	Absorption %	Loaf* Volume cc	Texture[1]	Crumb Color[2]	Crust[3]	Symmetry[4]
384	Siberian	9.2	53.4	465	66.6	124	7.0	6.5 g-y	D	3.5 o
382	Siberian	9.4	52.2	440	66.6	122	6.5 o	6.0 g-y	D	3.0 o
383	Siberian	12.1	54.4	520	69.6	130	6.5 o	7.0	D	3.5 o
49	Turkey	14.6	52.1	700	69.6	149	7.5	8.0	S	4.5 o
46	Nebred	14.8	52.0	680	66.6	155	7.5	8.0	S	4.5 o
47	Tenmarq	15.5	51.1	720	68.6	134	7.0	7.5	S	4.0 o
48	Blackhull	15.9	50.7	650	66.6	137	6.5 o	8.0	S	4.0 o
50	Chiefkan	15.9	51.6	680	68.6	137	3.0 C,o	7.0	S	4.0 o
891	Potato				71.6	115	3.0 C,o	6.0 g-y	P-D	2.0 o
	Commercial wheat starch				69.6	98	3.0 C,o	6.0 g-y	P-D	2.0 o
	Commercial corn starch				71.6	92	3.0 C,o	4.0 g	P-D	1.0 o
	Commercial rice starch				83.6	98	3.5	5.5 g-y	P-D	2.0 o

* Micro-method used

[1] Texture: o—open; C—coarse; c—close. Perfect score—10
[2] Color: y—yellow; g-y—gray-yellow; g—gray. Perfect score—10
[3] Crust: D—dull; S—satisfactory; P—pale.
[4] Symmetry: o—overoxidized. Perfect score—10.

Nebred starch gave the best loaf. With the Siberian wheats differences in baking quality were much more pronounced in the case of the original flours than with the corresponding starches, indicating that the difference in strength in these Siberian wheat samples lies in their relative wheat protein content. The commercial starches all gave inferior loaves with little difference between wheat, corn and rice. On the other hand, potato starch gave rather good results.

In summarizing these investigations, the author cautions against placing complete reliance upon the results since, as he points out, the starch and gluten used in these bakes have been removed from their natural environment and may have been altered in their properties by separation from the flour. Furthermore, some of the flour constituents which may have a bearing upon quality are removed in the gluten washing process.

CHAPTER II

FATS AND OILS

A second large class of organic compounds of immense importance in nature comprises the fats and oils. Like the carbohydrates, true fats also are composed solely of carbon, hydrogen and oxygen. However, their molecular structure differs decidedly from that of carbohydrates and their properties are correspondingly distinct. One essential structural difference between fats and carbohydrates is that in a molecule of fat the proportion of oxygen in relation to hydrogen and carbon is far less than in a carbohydrate. Another important difference is that fat molecules are limited in their configuration to a relatively few forms only in contrast to the great variety possible in the glucosyl polymers.

The terms "fats" and "oils" do not refer to basically different substances but are merely indicative of the physical state of otherwise closely related substances at ordinary temperatures. A product which at normal room temperature is liquid is called an oil, whereas one which is solid or semi-solid is referred to as a fat. No sharp division between the two can be made since all oils, when sufficiently cooled, become solid, and all fats liquefy at even moderately elevated temperatures. As will be pointed out subsequently, solid fats contain a relatively large proportion of liquid oil.

An insight into the basic composition of fats may perhaps best be gained by examining the molecular structure of a common animal fat, tripalmitin. It has the formula $C_{51}H_{98}O_6$. At first glance this formula appears to indicate a highly complex structure, but on analysis it will be found to be relatively simple. One obvious fact it reveals is that in comparison to carbohydrates the fats have a very low oxygen content. When tripalmitin is subjected to complete hydrolysis, that is, when it is split apart, two types of smaller molecules are obtained, namely one molecule of a substance called glycerol, more commonly known as glycerin, and three molecules of the fatty acid known as palmitic acid. Glycerol, which belongs to the group of aliphatic alcohols, is a colorless, viscous sweet liquid. It possesses considerable ability to take up moisture and is for this reason used to some extent in baking to retard the drying out of baked goods. Its use is limited chiefly to the production of cakes and

sweet goods (*13*). The chemical formula of glycerol, or glycerin, is

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H---C---OH} \\
| \\
\text{H---C---OH} \\
| \\
\text{H---C---OH} \\
| \\
\text{H}
\end{array}
$$
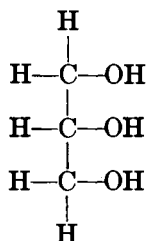
Palmitic acid is a so-called saturated fatty acid and is the most widely distributed member of this group of substances in nature, occurring in nearly all animal and vegetable fats. It has the following chemical formula:

$$
\text{H---}\overset{\displaystyle\text{H}}{\underset{\displaystyle\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{---}\overset{\text{O}}{\underset{}{\text{C}}}\text{---OH}
$$
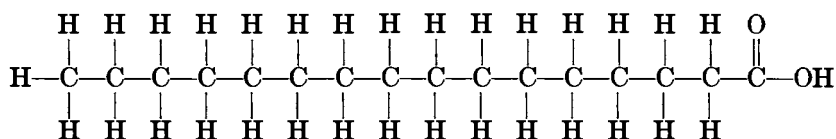
It thus constitutes essentially a chain composed of 16 carbon atoms in which one of the end carbons has 3 hydrogen atoms attached to it, the other end carbon forms a carboxyl group $\left(\text{---}\overset{\displaystyle\text{O}}{\overset{||}{\text{C}}}\text{---OH}\right)$, while the principal part of the chain consists of CH_2 groupings.

The hydrolysis of tripalmitin thus proceeds as follows:

| 1 molecule tripalmitin | 3 molecules water | 1 molecule glycerol | 3 molecules palmitic acid |
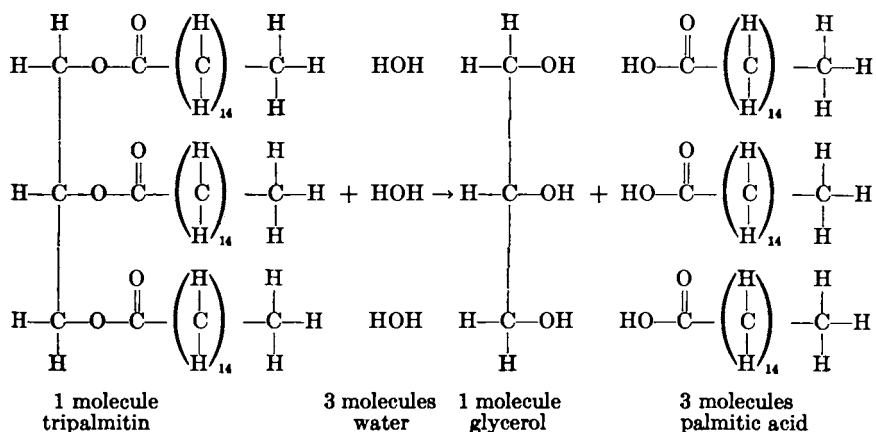
Since the above reaction is reversible, tripalmitin may be considered a condensation product formed by the union of one molecule of glycerol

with three molecules of palmitic acid. In the process, three molecules of water are freed.

The above analysis, with tripalmitin used merely as an example, holds true of all fats and oils. Fats may therefore be generally defined as glycerides containing three fatty acid radicals, or triglycerides. If the three fatty acids are of the same kind, the fat is a simple triglyceride. Tripalmitin is an example of such a simple triglyceride. If the fatty acids are different, as is normally the case in naturally occurring fats, the product is called a mixed glyceride.

Fats which are only partially hydrolyzed will contain so-called monoglycerides and diglycerides, that is, glycerides which contain only one and two fatty acid radicals, respectively. In the case of tripalmitin, such partial hydrolysis will result in products of the following type:

$$
\begin{array}{cc}
\text{H} & \text{H} \\
| & | \\
\text{H---C---OH} & \text{H---C---OH} \\
| & | \\
\text{H---C---palmitic acid} & \text{H---C---palmitic acid} \\
| & | \\
\text{H---C---OH} & \text{H---C---palmitic acid} \\
| & | \\
\text{H} & \text{H} \\
\text{Mono-palmitin} & \text{Di-palmitin}
\end{array}
$$
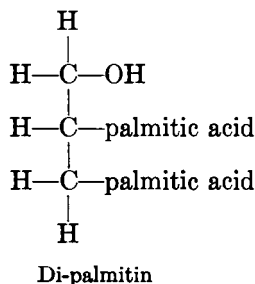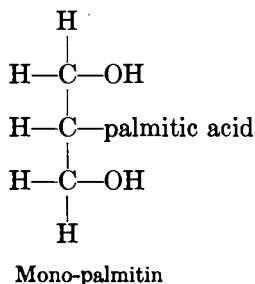
These products contain free hydroxyl groups (OH) which are relatively reactive. The analytical determination of hydroxyl groups in a fat gives an indication of the degree of hydrolysis which the fat has undergone.

THE FATTY ACIDS

The characteristics of fats are determined by their component fatty acids, which constitute from 94 to 96 percent of the total molecular weight of the fat and also comprise the reactive portion of the molecule. Most normally occurring fatty acids are straight hydrocarbon chains with a single carboxyl group ($-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OH}$) attached to one end. Except for isovaleric acid, they contain an even number of carbon atoms which range in number from 4 to 26. Individual acids differ from each other principally in the length of their carbon chain and the number and position of double bonds between the carbon atoms.

Fatty acids in which all carbon atoms are combined with two hydrogen

atoms and which therefore contain no double bonds are called saturated. The carbon chain of saturated acids is of the following order:

$$
\begin{array}{ccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | & | & | & | \\
-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}- \\
| & | & | & | & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H}
\end{array}
$$
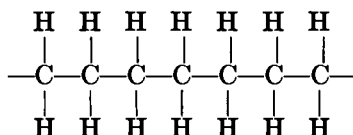
Fatty acids which contain double bonds are called unsaturated. These contain pairs of adjacent carbon atoms of which each member is joined to only one hydrogen atom and the degree of unsaturation depends upon the number of such carbon atoms present in the chain. Double bonds provide points in the molecule for the addition of oxygen, hydrogen, iodine, or other reactive substances, which accounts for the term "unsaturated." The introduction of double bonds into a fatty acid also results in a much more pronounced lowering of the melting point than is associated with a reduction in the length of the carbon chain; hence the melting point of a fat or oil is in general an indication of its degree of unsaturation. The structure of such an unsaturated chain is as follows:

$$
\begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | \\
-\text{C}-\text{C}=\text{C}-\text{C}- \\
| & & & | \\
\text{H} & & & \text{H}|
\end{array}
$$
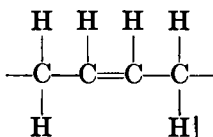
Saturated Fatty Acids. The saturated fatty acids listed in the following table have been identified as constituents of fats.

TABLE 2. THE NATURALLY OCCURRING FATTY ACIDS

Acid	No. of C atoms	Formula
Butyric	4	$CH_3(CH_2)_2COOH$
Isovaleric	5	$(CH_3)_2CHCH_2COOH$
Caproic	6	$CH_3(CH_2)_4COOH$
Caprylic	8	$CH_3(CH_2)_6COOH$
Capric	10	$CH_3(CH_2)_8COOH$
Lauric	12	$CH_3(CH_2)_{10}COOH$
Myristic	14	$CH_3(CH_2)_{12}COOH$
Palmitic	16	$CH_3(CH_2)_{14}COOH$
Stearic	18	$CH_3(CH_2)_{16}COOH$
Arachidic	20	$CH_3(CH_2)_{18}COOH$
Behenic	22	$CH_3(CH_2)_{20}COOH$
Lignoceric	24	$CH_3(CH_2)_{22}COOH$
Cerotic	26	$CH_3(CH_2)_{24}COOH$

As the number of carbon atoms increases in the acids, their melting and boiling points show a correspondingly progressive increase. Thus butyric acid, which has the shortest carbon chain, has a melting point of −8° C. (17.6° F.), caproic acid with the next shortest even numbered chain −1° C. (30.2° F.), caprylic acid 16° C. (60.8° F.), capric acid 31.3° C. (88.3° F.), etc. Cerotic acid, the longest chain acid, has a melting point of 84.2° C. (183.5° F.). Isovaleric acid with its odd numbered chain forms an exception, its melting point being at the extremely low temperature of −51° C. (−59.8° F.).

The saturated acids vary considerably in their distribution in natural fats. The most widely distributed acid, as already pointed out, is palmitic acid which occurs in practically all known fats and oils in amounts of 6-8 percent and is a major constituent of lard and some vegetable oils. On the other hand, butyric acid occurs naturally only in milk fats, where it represents some 2-4 percent by weight of the total fatty acids. Caproic acid is also largely limited to milk fats, occurring in them in similar amounts. Caprylic and capric acids occur in amounts of 1-8 percent in milk fats and in coconut and palm kernel oils. Lauric acid constitutes some 2-6 percent of milk fats, and is present in amounts of 40-50 percent in palm kernel oils. Myristic acid seldom exceeds 2 percent of various seed oils and animal fats; however, it is present to an extent of 18-20 percent in milk fats and may constitute 70-80 percent of nutmeg butter. Stearic acid is also quite widely distributed; it constitutes some 8 percent of lard. Arachidic, behenic, and lignoceric acids usually occur only in traces.

Unsaturated Fatty Acids: Unsaturated fatty acids with fewer than 10 carbon acids are unknown in nature, and acids containing 10, 12 and 14 carbon atoms occur only in traces and in a few fats. Unsaturated fatty acids whose structure has been established are listed in Table 3.

Palmitoleic acid occurs fairly widely distributed, but is most abundant in marine oils and fats. As is apparent from the table, the majority of fatty acids of known structure contain 18 carbon atoms. They differ, however, both in the number and position of their double bonds which accounts for their varying properties. The simplest, and at the same time most widely distributed, is oleic acid which contains one double bond at the center of the carbon chain. It occurs in all fats and oils, being the chief acid in milk fats, lard and tallow. It accounts for some 20 percent or more of the total fatty acids in such important oils as olive oil (76-86 percent), peanut oil, corn oil, palm oil, and others. Linoleic acid, which contains two double bonds, occurs only in traces in animal fats, and in vegetable fats is invariably associated with oleic acid. It accounts for

TABLE 3. UNSATURATED FATTY ACIDS

Acid	No. of C atoms	Formula
Decylenic	10	$CH_2\!\!=\!\!CH(CH_2)_7COOH$
Dodecylenic	12	$CH_3CH_2CH\!\!=\!\!CH(CH_2)_7COOH$
Palmitoleic	16	$CH_3(CH_2)_5CH\!\!=\!\!CH(CH_2)_7COOH$
Oleic	18	$CH_3(CH_2)_7CH\!\!=\!\!CH(CH_2)_7COOH$
Ricinoleic	18	$CH_3(CH_2)_5CH(OH)CH_2CH\!\!=\!\!CH(CH_2)_7COOH$
Petroselinic	18	$CH_3(CH_2)_{10}CH\!\!=\!\!CH(CH_2)_4COOH$
Vaccenic	18	$CH_3(CH_2)_5CH\!\!=\!\!CH(CH_2)_9COOH$
Linoleic	18	$CH_3(CH_2)_4CH\!\!=\!\!CHCH_2CH\!\!=\!\!CH(CH_2)_7COOH$
Linolenic	18	$CH_3CH_2CH\!\!=\!\!CHCH_2CH\!\!=\!\!CHCH_2CH\!\!=\!\!CH(CH_2)_7COOH$
Eleostearic	18	$CH_3(CH_2)_3(CH\!\!=\!\!CH)_3(CH_2)_7COOH$
Licanic	18	$CH_3(CH_2)_3(CH\!\!=\!\!CH)_3(CH_2)_4CO(CH_2)_2COOH$
Parinaric	18	$CH_3CH_2(CH\!\!=\!\!CH)_4(CH_2)_7COOH$
Tariric	18	$CH_3(CH_2)_7C\!\!\equiv\!\!C(CH_2)_7COOH$
Gadoleic	20	$CH_3(CH_2)_9CH\!\!=\!\!CH(CH_2)_7COOH$
Arachidonic	20	$CH_3(CH_2)_4(CH\!\!=\!\!CHCH_2)_4(CH_2)_2COOH$
Cetoleic	22	$CH_3(CH_2)_9CH\!\!=\!\!CH(CH_2)_9COOH$
Erucic	22	$CH_3(CH_2)_7CH\!\!=\!\!CH(CH_2)_{11}COOH$
Selacholeic	24	$CH_3(CH_2)_7CH\!\!=\!\!CH(CH_2)_{13}COOH$

a considerable portion in the more unsaturated oils, such as soybean oil, linseed oil (25-40 percent) cottonseed oil (40-45 percent), etc. Linolenic acid is the most common fatty acid containing three double bonds. It is the major constituent of linseed oil and occurs in most seed fats. Eleostearic acid is limited almost entirely to tung oil of which it constitutes some 80 percent. The only 18 carbon acid to have four double bonds is parinaric acid which has been isolated from the seed oil of only one species, Parinarium laurium. The fatty acids containing 20 to 22 carbon atoms and four or more double bonds occur chiefly in marine oils. Erucic acid, a 22 carbon atom acid with only one double bond is prevalent in the seed oils of rape, mustard, wallflower and others. Selacholeic acid occurs principally in fish oils. Fatty acids of unusual structure include the rare tariric acid which contains a single triple bond; ricinoleic acid, the main constituent of castor oil, which has an OH group substituted for a hydrogen atom at the 12th carbon atom; and licanic acid in which an oxygen atom replaces two hydrogen atoms at the 4th carbon.

While the number of different known fatty acids is considerable, only a relatively few are normally present in significant amounts in edible fats and oils. In fact, many important fats contain as their principal constituents only the four most common acids, namely palmitic, stearic, oleic and linoleic. The characteristics of a fat are usually unaffected by the presence of minor quantities of a fatty acid, except when the minor

fatty acid is highly unsaturated, in which case it may impair the fat's stability because of the pronounced susceptibility of the unsaturated constituent to atmospheric oxidation.

Classification of Fats and Oils. Fats and oils may be classified into the following groups, based upon their industrial utilization: (1) The *milk fats* derived from the milk of domesticated animals. They are rather similar in composition, containing oleic, palmitic, and stearic acids as their principal constituents, in addition to small amounts each of most of the low molecular weight acids, as well as of several of the unsaturated acids with 10 to 16 carbon atoms containing one double bond. (2) The *lauric acid fats,* obtained from the coconut palm, the oil palm, babassu, etc. They are so called because of their exceptionally high lauric acid content, which averages 40 to 50 percent of their total fatty acids. These fats also contain small amounts of such saturated acids as caprylic, capric, myristic, palmitic and stearic, while their unsaturated acids are limited to minor amounts of oleic and linoleic acids. Because of their high degree of saturation and low melting point, they constitute desirable edible fats for certain purposes. (3) The *vegetable butters,* represented by cocoa butter. They are similar to the lauric acid group in possessing a rather narrow temperature range over which they soften and melt. They consist of more than 50 percent of saturated fatty acids with 14 to 18 carbon atoms; their principal unsaturated acids are oleic and linoleic acids. (4) The *animal fats,* such as lard and tallow. These possess a high content of palmitic and stearic acids and a very low content of oleic and linoleic acids. Their rather extended plastic range is imparted by their relatively high proportion of fully saturated glycerides. (5) The *oleic-linoleic acid fats,* which include such oils as cottonseed, peanut, corn, olive, and others. They comprise the largest of the various groups. Their principal constituents are the two unsaturated fatty acids from which they derive their designation, and their saturated acid content seldom exceeds 20 percent. (6) The *eruric acid fats* include, among others, mustard and rape seed oils. They are seldom used for edible purposes. (7) The *linolenic acid fats,* of which soybean oil is an important member, contain linolenic acid, in addition to oleic and linoleic acids. Except for soybean oil, most oils of this group are used primarily in paint manufacture. The remaining groups, of little interest to bakers, include (8) the *conjugated acid fats* (tung oil, oiticica oil) used exclusively in the manufacture of certain varnishes and enamels because of their pronounced drying properties, (9) the *marine oils* (fish and whale oils) and (10) the *hydroxy acid oil,* the sole member of this group being castor oil.

THE COMPOSITION OF FATS

In discussing the composition of fats, no attempt will be made to cover all of the classes of fats and oils listed above. A large number of oils belong to the category of inedible products whose industrial utilization is confined to the manufacture of soaps, paints, enamels, lubricants, and other specialized applications. Even among the edible oils only a relatively few are of outstanding commercial importance and of these again a still more limited number is of direct interest to the baker as constituting materials which he uses in the production of baked goods. The following discussion will therefore be limited to those fats which he uses either in their more or less natural state, such as butterfat and lard, or which form important constituents of hydrogenated shortenings.

Butterfat. Butterfat is characterized by the great variety of its component fatty acids, many of which have been identified only recently. Its fatty acid composition is given in the following table by Hilditch and Jasperson (*14*).

TABLE 4.   FATTY ACID COMPOSITION OF
BUTTERFAT

Fatty acids	Percent by weight
Butyric............................	3.7
Caproic...........................	1.7
Caprylic...........................	1.0
Capric.............................	1.9
Lauric.............................	2.8
Myristic...........................	8.1
Palmitic...........................	25.9
Stearic............................	11.2
Arachidic.........................	1.2
Decylenic.........................	0.1
Dodecylenic.......................	0.2
Myristoleic........................	0.6
Palmitoleic........................	3.4
Oleic..............................	32.8
Linoleic...........................	3.7
C_{20} and C_{22} unsat...................	1.7

The values shown are to be considered as average only since it has been found that butterfat may vary considerably in its fatty acid composition, depending upon the season of the year, the type of ration fed to the animal, and the animal itself. It will be noted that quantitatively the unsaturated oleic acid is present in largest amount, followed by the

saturated palmitic, stearic and myristic acids. On the whole, the saturated acids predominate, being present to the extent of some 57.7 percent as against 42.5 percent of unsaturated acids. Hilditch and Sleightholme (*15*) have reported studies on the degree of saturation and unsaturation of the triglycerides of butterfat. They found that 27.2 percent of the glycerides consist of saturated fatty acids only (trisaturated), 33 to 52 percent contain two saturated and one unsaturated acids (disaturated-monounsaturated), 39.8 to 0 percent have one saturated and two unsaturated acids (monosaturated-diunsaturated), and up to 19 percent of glycerides consist of unsaturated acids only (triunsaturated). Butterfat contains the largest amount of butyric acid of any known fat and is in general characterized by the low average molecular weight of its fatty acids. Other additional average characteristics of butterfat are as follows: density at 60° C. (140° F.), 0.887; melting point, 38° C. (100.4° F.); titer (which is the temperature representing the initial solidifying point of a fat), 34° C. (93.2° F.); unsaponifiable matter, 0.4 percent (*16*). From a nutritional viewpoint, butterfat, in addition to its high calorie value, is an important source of vitamin A, which is present in amounts ranging on an average from 5 to 9 μg per gram of butter. It also contains from about 2 to 7.6 μg of carotene per gram which is partially converted into vitamin A in the human body. Both the vitamin A and the carotene contents are normally highest in the summer when the animals have access to green pastures and lowest in the winter. Butter is also a significant source of vitamin D, whose content is also subject to a similar seasonal variation.

Coconut Oil and Palm Kernel Oil. Coconut oil, and the lauric acid oil group in general to which it belongs, are distinguished by their high content of low molecular weight fatty acids. This accounts for their relatively low melting point which, in the case of coconut oil, is near 76° F. Coconut oil also has an exceptionally short plastic range, that is, it does not soften gradually as the temperature is increased but changes quite abruptly from the solid to the liquid state. This characteristic is attributable to the fact that about 75 percent of its total fatty acids consist of lauric, myristic, and palmitic acids, all of which melt within the rather narrow temperature range of 44° to 63° C. (111.2°-145.4° F.), showing thus a difference of only 19° between the upper and lower limits (*16*). The corresponding temperature range between the highest and the lowest melting fatty acids present in the more plastic fats averages 70° and higher. Since the melting point of fatty acids governs that of the glycerides which they form, it will be seen that the narrower the range is between the melting temperatures of the major fatty acids of a fat, the shorter will be its plastic range. Furthermore, coconut oil can be changed

relatively little in its melting point and consistency by hydrogenation since it contains only 9 percent of combined oleic and linoleic acids which are affected by hydrogenation, the remaining 91 percent of saturated acids remaining unaffected. Fully hydrogenated coconut oil has a melting point of about 111° F. Its characteristic odor and flavor are due to the presence of soluble and volatile free fatty acids which, in a high grade oil, should not exceed 3 percent. The narrow plastic range of coconut oil greatly restricts its use in edible products. Thus it usually represents only a minor ingredient in shortening, but is used to advantage in the production of confections where its short plastic range constitutes a desirable attribute. Palm kernel oils are quite similar to coconut oil in composition, appearance, plastic range, etc., and are used much for the same purposes. The fatty acid composition of coconut and palm kernel oils in percent by weight is given in the following table:

TABLE 5. FATTY ACID COMPOSITION OF COCONUT AND PALM
KERNEL OILS IN PERCENT BY WEIGHT

Fatty acid	Coconut oil[1]	Palm kernel oil[2]
Caproic	0.8	—
Caprylic	5.4	2.7
Capric	8.4	7.0
Lauric	45.4	46.9
Myristic	18.0	14.1
Palmitic	10.5	8.8
Stearic	2.3	1.3
Arachidic, etc.	0.4	—
Oleic	7.5	18.5
Palmitoleic	0.4	—
Linoleic	—	0.7

[1] H. E. Longenecker, *J. Biol. Chem. 130,* 167 (1939).
[2] G. Collin and T. P. Hilditch, *J. Soc. Chem. Ind. 47,* 261 (1928).

Cocoa Butter. Cocoa butter belongs to the group of vegetable butters which are the only seed fats that are solid at ordinary temperatures. Furthermore, they are characterized by a still narrower temperature range in which they melt than are the lauric acid fats. In their case, however, the short melting range is due not to the presence of low molecular weight fatty acids, but to a preponderance of glycerides of nearly the same melting point. Bailey (16) points out that over 70 percent of the glycerides of cocoa butter, for example, are composed of a single oleic acid radical in combination with stearic or palmitic acid, or both. Cocoa butter, because it lacks greasiness when in the solid state, and melts at a temperature below that of the human body, makes an ideal

fat for coating confections for which purpose it is usually blended with chocolate. In its natural state, cocoa butter is a pale yellow solid possessing the characteristic odor and taste of the cocoa bean. It melts rather sharply at a temperature of about 93-95° F. The fatty acid composition of cocoa butter is given in the following table which indicates that this fat consists in the main of only four different types of fatty acids (*17*).

TABLE 6.   FATTY ACID COMPOSITION OF COCOA
BUTTER IN PERCENT BY WEIGHT

Fatty acid	Percent by weight
Palmitic	24.4
Stearic	35.4
Oleic	38.1
Linoleic	2.1

Lard. Lard is used rather extensively in bread baking and in the production of some cake products. It is also used as a primary ingredient of neutral shortenings. Lard reaches the market in several different grades, depending upon the part of the animal from which it is derived and also the method used in its rendering. Prime steam lard, obtained from the fat from all parts of the animal, represents the major portion of lard produced in this country. Leaf lard is rendered dry from the internal fat of the hog and is firmer than the other lards. Neutral lard, rendered wet from selected stock, is no longer an important item of commerce. Kettle rendered lard is produced in large amounts from leaf and back fats.

TABLE 7.   FATTY ACID COMPOSITION OF LARD

Fatty acid	Percent in weight
Myristic	1.3
Palmitic	28.3
Stearic	11.9
Myristoleic	0.2
Palmitoleic	2.7
Oleic	47.5
Linoleic	6.0
C_{20} and C_{22} unsat.	2.1

Lard varies considerably in its composition, consistency and general characteristics according to the type of feed given the hogs and the part of the animal from which the lard is obtained. Thus the lard from hogs fed on soybeans or peanuts is much softer than lard from corn fed hogs.

Also, lard derived from the internal leaf fat of the animal is much firmer than lard from other parts of the animal. The modern practice of adding hydrogenated lard "flakes" to regular lard has enabled the production of lards of standardized plasticity. An average fatty acid composition of lard is reproduced in Table 7 from the data by Hilditch, Lea, and Pedelty (*18*).

Cottonseed Oil. Cottonseed oil, which is an important representative of the oleic-linoleic acid group of oils, derives its main significance for the baker from the fact that it constitutes the major constituent of most hydrogenated shortenings used in the production of cakes and cookies. The composition of the oil varies markedly in accordance with the region in which the cotton was grown. Thus Texas cottonseed oil is usually more unsaturated than oil obtained from the lower Mississippi valley. The fatty acid composition of a typical sample of cottonseed oil is given in the following table which reproduces values obtained by Hilditch and Maddison (*19*). It will be noted that cottonseed oil contains about 25 percent of saturated fatty acids and that the two major unsaturated fatty acids are linoleic (47.8 percent) and oleic (22.9 percent).

TABLE 8.   FATTY ACID COMPOSITION OF COTTON-
SEED OIL

Fatty acid	Percent by weight
Myristic	1.4
Palmitic	23.4
Stearic	1.1
Arachidic	1.3
Myristoleic	0.1
Palmitoleic	2.0
Oleic	22.9
Linoleic	47.8

Peanut Oil. Peanut oil, like cottonseed oil, belongs to the group of oleic-linoleic acid oils and is therefore similarly characterized by containing some 75-80 percent of oleic and linoleic acids. It is utilized extensively in the production of high grade all-hydrogenated shortenings in which it may be used interchangeably with cottonseed oil. The fatty acid constituents of peanut oil are given in Table 9 cited by Bailey from the data by Hilditch and co-workers (*16*).

Soybean Oil. Soybean oil, which is a representative member of the group of linoleic acid oils, is of some importance as an ingredient of all-hydrogenated shortenings in which it may be present in amounts of 25

TABLE 9. FATTY ACID COMPOSITION OF PEANUT
OIL

Fatty acid	Percent by weight
Palmitic	8.3
Stearic	3.1
Arachidic	2.4
Behenic	3.1
Lignoceric	1.1
Oleic	56.0
Linoleic	26.0

percent or less of the total shortening weight. It is not used in higher proportions, at least not in high grade shortenings, because of its tendency to undergo flavor reversion, that is, to return to its original beany odor and flavor even after complete deodorization by means of high temperature steam. Also it has a somewhat disagreeable odor at frying temperatures. The composition of the oil varies markedly, depending upon origin. According to values gathered by Bailey (16), soybean oil contains from 11.9 to 13.5 percent saturated fatty acids, 11.5 to 60 percent oleic acid, 25 to 63 percent linoleic acid, and 2.9 to 12 percent linolenic acid.

Nonglyceride Components. Pure triglycerides are colorless, odorless and tasteless. The characteristic colors and flavors of the oils and fats of commerce are due to small amounts of impurities naturally associated with the fats. In some instances, such as butter, lard, olive oil and others, these characteristic odors and flavors are desirable. In other fats, such as the oils of soybean, peanut, cottonseed, whale, fish, etc., the presence of the associated flavors and odors is generally objectionable and these oils, if used for the production of neutral hydrogenated shortenings, must be subjected to deodorization treatments before they become acceptable to the consumer.

Among the impurities present in vegetable oils especially are substances possessing pronounced antioxygenic properties which act to retard the onset of deterioration in the oils. Among naturally occurring antioxidants are the tocopherols, which are identical with vitamin E, cephalin, hydroquinone and pyrogallol. If the fats are highly purified, causing the removal of antioxidants, their stability is proportionately impaired. This deficiency in stability is usually corrected by the artificial addition of antioxygenic substances, such as the tocopherols, gum guaiac, nordihydroguaiaretic acid, and other substances.

Fat-bearing tissue of both animal and plant origin always contains

certain so-called lipolytic enzymes which are capable in the presence of moisture of splitting the fat molecule into glycerol and fatty acids. It is normally impossible to process the raw fats rapidly enough to prevent all enzymatic action so that all fats and oils contain a certain amount of free acids and glycerol. While this amount is normally minute in high grade commercial products, it may be as high as 10 percent in those cases where a considerable time has been allowed to elapse between the initial and final processing treatments.

SPOILAGE OF FAT

The spoilage of fats differs essentially from the most prevalent form of food deterioration in that it is seldom caused by bacterial agents but involves oxidation by atmospheric oxygen. While the reactions leading to true rancidity are as yet not clearly understood, the initial step appears to be the addition of oxygen at the double bonds resulting in the formation of peroxides. The peroxides are quite unstable and decompose into aldehydes of medium molecular weight which are the compounds actually responsible for rancid odor and flavors. The reaction in its essential form may be represented as follows:

$$CH_3(CH_2)_n-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-R + O_2 \rightarrow CH_3(CH_2)_n-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{|}}{C}}-R \rightarrow CH_3(CH_2)_n-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}} + \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-R$$

| Unsaturated glyceride | Peroxide | Aldehydes |
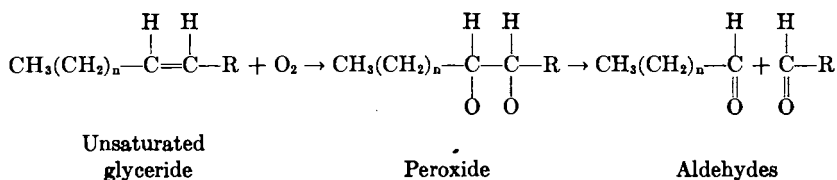
The view that rancidity development is a self-perpetuating process is gaining general acceptance. "According to this so-called chain reaction theory, a molecule of fat and a molecule of oxygen are able to unite to form a peroxide only after one or the other, or both, are activated by the absorption of a quantum of energy. This energy may be radiant energy, proceeding from heat or light applied to the oil, or chemical energy, derived from molecules of reactive substances in the oil which are at a high energy level. After union has occurred and peroxide formation is completed, the activating energy may be released and made available for the activation of a new molecule or molecules, to form a peroxide. A chain of reactions is thus set up, and the initial absorption of a single unit of energy will result in the formation of a great number of peroxide molecules, unless the chain is broken by absorption of the activating energy in extraneous reactions" (16). Antioxidants are thought to exert their stabilizing effect by absorbing the activating energy and thereby removing it from the chain reaction, becoming themselves oxidized in the process.

The development of rancidity has been shown to take place in two distinct phases. There is a so-called induction period in which oxidation proceeds at a very slow rate and in which no perceptible rancid odor develops. After a certain critical point is reached, the rate of oxidation is rapidly accelerated and the characteristic rancid odor makes its appearance.

While the ease with which a fat will turn rancid, that is, become oxidized, depends mainly upon its degree of unsaturation, it is also considerably influenced by the presence of accessory substances which may act as antioxidants or pro-oxidants. It has not been definitely established whether pro-oxidants occur naturally in fats, but all fats and oils contain antioxidants. These substances are effective in extremely minute concentrations on the order of a few parts per million. Some of the antioxidants are discussed in the following paragraphs. Pro-oxidants include various metals, the most active being copper, which therefore should not be used in equipment intended for processing or storing fats.

Fat deterioration may also be caused by enzymatic activity and here the type of rancidity developed depends upon the kind of enzymes present. For example, lipases cause hydrolysis of the fat to free fatty acids and glycerin. Catalase has been reported to act as an inhibitor of oxidation, whereas lipoxidase promotes oxidation. Certain microbial enzymes are capable of producing odoriferous ketones from saturated acids of a molecular weight lower than that of myristic acid leading to the designation of this type of rancidity as "ketonic rancidity." Light is a powerful catalyst of oxidative rancidity and may induce a type of chemical change that differs from ordinary oxidative rancidity. Fats exposed to ultraviolet or diffused daylight acquire a characteristic odor and flavor that is readily distinguishable from that caused by atmospheric oxidation in the absence of light. This effect of light has been designated as "light-induced rancidity." The usual anti-oxidants have little or no influence on the development of this particular off-flavor (*20*).

STABILIZATION OF FATS

Recent years have seen an increasing emphasis being placed upon the keeping quality of fats for use in baked products. Improved stability is generally obtained in two different ways, namely by the use of antioxidants and by hydrogenation. A widely used method for measuring fat stability in the laboratory is the Active Oxygen Method or Swift method (*21*) which involves the acceleration of oxidation of the fat by blowing it with air at a temperature of slightly over 200° F. The results are expressed in a number which represents the duration in hours the fat requires to become definitely rancid. The end point is determined or-

ganoleptically and verified by titration of the peroxides formed in the sample. The peroxide value at the end point varies with different fats. McKinney and Jacobson (*22*) give the following values (M.E. being the milli-equivalents of peroxide per 1000 grams of fat):

Lard	20 M.E.
Hydrogenated lard	40 M.E.
Oleo oils	60 M.E.
Hydrogenated vegetable fats	80 M.E.

Hydrogenation has a pronounced effect upon stability. Crude oils, such as cottonseed oil, require considerable refining and bleaching to render them suitable for shortening use. This refining treatment, however, greatly reduces the stability of the fat toward oxidation by removing the naturally occurring antioxidants. When the refined oils are subsequently hydrogenated to produce shortening, the stability is again increased. A similar trend is observed with lard and other animal fats with the difference, however, that these fats are almost totally deficient in antioxidant content to begin with. The change in stability which fats undergo as a result of their treatment is indicated in the following table (*22*).

TABLE 10. CHANGE IN STABILITY OF FATS DUE TO HANDLING

Vegetable Oil	SKQ*	Lard	SKQ*
Crude...................	50	Rendered..............	18
Refined................	10	Refined..............	8
Hydrogenated &		Hydrogenated &	
Deodorized...........	90	Deodorized..........	22

* SKQ = Swift Keeping Quality in hours.

Different shortenings have been shown to possess widely varying keeping qualities. Thus McKinney and Bailey (*23*) subjected a number of fats to accelerated oxidation tests with the results recorded in Table 11.

Whereas only a few years ago the accepted ultimate limit of stability for vegetable oils was 40 to 50 hours as measured by the Swift method, recent improvements in refining and hydrogenation have increased this value to 80 to 90 hours and in exceptional cases to 100 to 130 hours without the use of antioxidants. Animal fats are less susceptible to such improvement, the maximum values obtained from them being still under 40 hours, hence the use of antioxidants is of much greater importance in their case than with vegetable oils.

A considerable number of substances have been found to exert a rancidity-retarding effect on fats and oils. Individual antioxidants vary

TABLE 11.   RESULTS OF ACCELERATED TESTS ON SEVERAL FATS

	Keeping Quality of Fat	
Shortening	Swift method* Hrs.	Schaal method** Days
Prime steam lard.............................	8	10
Prime steam lard plus 0.1% lecithin...........	9	11
Oleo oil......................................	10	12
Oleo oil plus 0.1% lecithin...................	60	65
Hydrogenated lard............................	22	26
Hydrogenated vegetable oil...................	70	70

* Exposes sample to 210° F.
** Exposes sample to 145° F.

considerably in their effectiveness with different fats. Thus soybean lecithin has a pronounced stabilizing effect upon oleo oil but is of no practical value in vegetable oils. Furthermore, some antioxidants are effective only in combination with another substance, called a synergist. The following example serves to show up such a synergistic effect. When ascorbic acid (vitamin C) is added in an amount of 0.005 percent to lard having a keeping quality value of 6 hours, no improvement in stability results. When 0.005 percent of nordihydroguaiaretic acid (NDGA) is added to this same lard, its keeping quality is increased to 27 hours. If, however, 0.005 percent increments of both of these substances are added to the lard, a keeping quality value of 78 hours results (*22*). Some antioxidants, such as gallic acid and isopropyl gallate, have their effectiveness completely destroyed by the heat treatment to which the fats are subjected during deodorization and must therefore be added after such treatment, while others, such as phosphoric acid, are greatly improved in their antioxygenic effect by such heat treatment and must be added prior to deodorization.

Antioxidants to be acceptable must be completely nontoxic in the amount used, colorless, odorless and tasteless. They must further be effective in minute concentrations. Among the more common antioxidants are soybean lecithin, the tocopherols, ascorbic acid, the gallates, gum guaiac, nordihydroguaiaretic acid, citric acid and tannic acid. The use of some of these is covered by patents. The most recent and by far the most important antioxidants used in present day lards and shortening are combinations of butylated hydroxy anisole (BHA), propyl gallate and citric acid. BHA is heat stable and for that reason is widely used in cracker lards, potato chip shortenings, and prepared mix shortenings.

Physical Requirements of Bakery Fats. In evaluating the suitability of a fat for baking use, two properties which generally receive pri-

mary consideration are the fat's organoleptic characteristics and its plastic range. Flavor and odor are obviously of great importance. Their proper evaluation requires considerable skill which is acquired only by prolonged and systematic practice. The flavor and odor standards for such fats as butter designed for bakery use and table use are not identical. Table butter should possess a flavor and odor which are mild but characteristic. Bakery butter normally requires a somewhat more pronounced flavor to have it imparted to the finished bakery product. However, a clear distinction must be made between butter flavor which is strong but clean and pleasant and one which derives its strength from incipient rancidity. Deodorized shortenings should be completely devoid of any flavor or odor whatsoever.

The plastic range, or the fat's consistency at different working temperatures, is of utmost importance to the fat's performance in baking. This plasticity or body of a fat can be best evaluated by penetration techniques carried out at a set of temperatures which usually include 50°, 70°, 80°, 90°, and 95° F. Creaming ability and emulsifying power of fats are at present determined by experimental baking tests carried out under standardized conditions.

While a fat, such as shortening, may appear to be a soft and homogeneous solid, it will be found upon examination under a microscope to consist of a mass of tiny individual crystals enmeshing a considerable proportion of liquid oil. It is this combination of solid and liquid which imparts a plastic character to shortening, as well as to other solid fats. Bailey (*16*), in discussing plasticity in fats, points out three conditions which are essential for plasticity in a material. First, it must consist of a solid phase and of a liquid phase, or the two must be capable of acting as solid and liquid. Secondly, the solid phase must be in a sufficiently fine dispersion for the mass to be held together by internal cohesive forces, without the solid particles being affected by gravitational force or permitting the liquid phase to seep from the mass. Thirdly, the two phases must be in proper proportion to each other, that is, the proportion of solid particles must be adequate to prevent the free flow of the mass, but not preponderant enough to form a rigidly interlocked structure.

The solid glyceride content of different plastic fats varies markedly at different temperatures. This is due to the fact that different glycerides possess different melting points so that certain proportions of glycerides which occur in a solid form at a lower temperature liquefy progressively as the temperature is increased. This accounts for the softening of the body of fats as the temperature rises. Bailey and co-workers (*16*) have investigated the relative proportions of solids and liquids in an average

all-hydrogenated shortening and have found the following estimated percentages of solid crystals:

At temperature of	Percent crystals
50° F. (10.0° C.)	52%
60° F. (15.6° C.)	40%
70° F. (21.1° C.)	30%
80° F. (26.7° C.)	21%
90° F. (32.2° C.)	16%

This group of investigators arrive at the conclusion that commercial fats are plastic and workable within a relatively broad range of solid glyceride content, which in the case of hydrogenated cottonseed oil appears to be approximately 15 to 45 percent.

QUALITY EVALUATION

There are a number of functional and quality considerations that enter into the selection of specific types of shortenings for baking purposes. Among the principal properties used to evaluate fats are their free fatty acid (FFA) content, flavor and odor characteristics, stability, color, and such functional qualities as shortening, creaming, emulsification and water absorption values. The free fatty acid content of a shortening may be indicative of the fat's quality. In undeodorized lards it discloses the care with which these fats were handled prior to and during rendering. According to Crapple (*24*) a FFA content of 0.5 percent or less is considered satisfactory in such lards. In deodorized shortenings the FFA content is a measure of the efficiency of deodorization and should not exceed 0.06 percent. This level, however, does not apply to emulsifier type shortenings containing mono- and diglycerides since the addition of these emulsifying agents introduces fatty acids. All deodorized shortenings should be bland in flavor and odor. The degree of blandness is generally employed as an important quality measure, and most shortening manufacturers maintain small panels of expert tasters to rate the shortenings on the basis of an arbitrary quality scale. The development of off-flavors in shortenings at any time constitutes a serious problem. The flavor stability of fats is determined by various accelerated aging tests which generally consist of holding the melted fat at an elevated temperature, with or without aeration, and noting the development of off-flavors or odors at regular intervals. These tests must be correlated with shelf tests simulating normal conditions of distribution, storage, and use. A shortening containing hydrogenated soybean oil might be perfectly bland prior to its use, but might acquire a strong reversion flavor during frying and impart it to the products being fried. Or the shortening may revert in the product after the latter has reached

the channels of distribution. The best procedure for testing the effect of the flavor of shortening on the flavor of the products made with it is to prepare product samples, store them for a period and under conditions normally encountered during distribution, and then submit them to an acceptance panel.

The stability or keeping quality of fats is a measure of their resistance to oxidation or the development of rancidity and determines the suitability of a given shortening for certain purposes. A shortening which tends to turn rancid within a short time obviously cannot be safely used in certain fried and baked products and in dry mixes that are liable to be stored for prolonged periods. Of the many so-called accelerated tests that have been developed for measuring the keeping quality of fats, the two most commonly used are the Active Oxygen Method described by King, Roschen and Irwin *(21)* and the 60° C. (140° F.) incubation test of Schaal. The latter consists essentially of determining the stability of the fat contained in a glass container kept at 60° C. in an oven. The method may also be applied to baked or fried goods. It is difficult, and often quite impossible, to predict shelf life of baked or fried goods from an accelerated test run on the shortening. Frequently two different shortenings may have essentially the same keeping quality as measured by any of the common accelerated tests yet show great variations in stability after being incorporated into a baked or fried product. Also, while most antioxidants have a marked improving effect on the stability of fats as measured by accelerated tests, very few of them carry through to the baked or fried goods. The most effective way to evaluate a shortening for stability on the shelf and in finished baked ⌐ ᵍds or dry mixes is to actually run long-term shelf tests simulating the . ᵢous conditions normally encountered during distribution. Shortenings possessing a pure white color are preferred over those with a grayish cast so that color assumes some importance.

Color can be regulated to a considerable extent by the crystallization, air or nitrogen content, and tempering, although the color of the oil must first be controlled. Most white shortenings have a color value of less than 2.0 Lovibond red units. Color may undergo some change on prolonged storage at elevated temperatures as a result of changes in the crystalline structure or the loss of air in the fat.

The functional qualities of shortening are generally tested by actual baking tests carried out under standardized conditions and ingredients. The shortening value of a fat, which is its ability to tenderize baked products, is commonly measured by the Bailey shortometer *(25)* by means of which the baking strength of standard crackers or pie crust is determined. Since factors other than shortening affect the breaking

strength, strict standardization and a fairly large number of tests are required to yield valid results. Creaming value, or the ability of shortening to take on air during the mixing operation, is of the utmost importance, especially in the production of certain types of cake, such as pound cake. The creaming value is most accurately determined by making a regular pound cake batter, but omitting the chemical leavener, and measuring the volume of one pound of the baked cake. If carried out under strictly standardized conditions, the test is readily reproducible. It is especially important to control the temperature of the batter which can be done with the aid of a water bath in which the mixing bowl is placed since the creaming value is affected by the temperature at which the batter is mixed. This procedure also permits the determination of the creaming range or temperature span over which a shortening will yield good creaming qualities. Emulsification value refers to the ability of the shortening to make a white layer cake of low flour content and high sugar and moisture contents. Again the only satisfactory test for emulsification value consists of making a high-sugar, high-moisture white layer cake under standardized conditions. Cake volume per pound is the criterion of value, with character of crust, grain and texture contributing to the evaluation. Good superglycerinated shortenings (cf. page 569) should produce cakes having volumes of 1,300-1,400 cc. per pound in addition to satisfactory top crust, a fine grain, silky texture and superior eating qualities. The ability of a shortening to take up water and hold it is a property that is of considerable importance in the making of certain types of cream fillings. This property can be readily measured by sled ly adding water to the shortening while it is being creamed in a la shratory mixer until the fat will no longer take up water. The amount of water absorbed is calculated in terms of percent of the weight of fat used. Superglycerinated fats will give values up to 800 percent, while other shortenings will range from 100 to 400 percent (*24*).

NUTRITIONAL FUNCTIONS OF FATS

Fats perform a number of important functions in the human organism. Together with the carbohydrates, the fats provide most of the energy expended in the living body. Their caloric value is exceptionally high, one gram of fat when burned in the body yielding 9 calories. By comparison, carbohydrates and proteins each provide only 4 calories when utilized as fuel by the organism. Fats therefore represent a highly concentrated fuel and it is in the form of fat that excess food ingested by man is stored for future use by his body. Fats and fatlike compounds play an important role in the structure of all cells. "The protoplasmic bounding-membrane of the cell contains fatlike compounds, as do also

intra-cellular membranes like that which bounds the nucleus. Special structures, like the sheaths about nerve fibers, also contain fatlike substances in abundance" (*26*). Fat is a poor conductor of heat and, deposited in quantities just under the skin, serves as an effective insulant.

While the body synthesizes fat from carbohydrates, it appears to be unable to produce certain essential unsaturated fatty acids (e.g. linolenic and linoleic) which must therefore be supplied by fats in the diet. Animals kept on a fat-free diet for prolonged periods of time develop a form of dermatitis and disorders of internal organs.

The comparative nutritive value of different fats has formed the subject of numerous studies and discussions. Certain natural fats, such as butterfat, owe their nutritional superiority over highly refined fats to their content in relatively important quantities of such fat-soluble vitamins as A and D. Careful investigations have shown that there is no significant difference in the digestibility of fats, except for those possessing a melting point considerably above body temperature which are less completely digested.

GLYCERIN (GLYCEROL)

Glycerin, or glycerol, is a sirupy, water-white, odorless liquid possessing a marked sweet taste. Although it has an oily feel, it has no other oily characteristics. According to its chemical composition it is classed as a triple alcohol with the following structural formula:

$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ H \end{array}$$
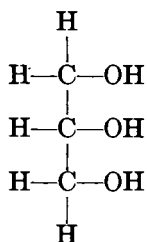
This formula will be recognized as an integral part of fats and oils which, in fact, represent triglycerides with the OH groups of the above formula being replaced by fatty acid radicals. Glycerin is produced by the hydrolysis of fats into glycerin and fatty acids and it is also a by-product of soap manufacture. Research has shown glycerin to be formed during yeast fermentation so that it actually occurs in minute amounts in all yeast-raised bakery goods. Furthermore, glycerin is present as a normal constituent in the human body, being liberated from dietary fats and oils upon their digestion. It thus represents a physiologically wholesome product which can be safely used as an additive to solid foods.

Glycerin possesses three characteristics that account for its use in food products generally and in bakery goods in particular. From the standpoint of baking the most important of these is its hygroscopicity. This property of attracting and retaining moisture makes the product a highly desirable ingredient in such products as cakes, cookies, etc., whose shelf life it prolongs to a marked degree. The second important characteristic of glycerin is its stabilizing function in oil-water emulsions in which it aids in maintaining permanency. This property also finds useful applications during creaming operations in baking. The third important property of glycerin is its solvent action. Glycerin is widely used in flavoring materials on the one hand, and in food colors on the other, being one of a relatively small number of solvents which are completely non-toxic. In baking, glycerin-dissolved flavoring compounds are retained better and the finished product has a stronger and fresher flavor. The flavor also receives more uniform distribution. Among important cake ingredients, glycerin has found widespread application in the packing of frozen egg yolk. Glycerin egg yolks contain from 5 to 7 percent glycerin which aids in prolonging their freshness and prevents the formation of gummy, lumpy particles. Glycerin derivatives are also used to some extent in frozen egg mixes where they are said to improve the emulsifying properties of the egg material.

In the bakery pure glycerin is used primarily in the production of cakes. Generally, the amounts added are quite small, ranging from less than 1 percent to a maximum of 2 percent in some formulas. The addition of glycerin tends to reduce evaporative losses during baking, improve the texture and sheen of the crumb and add to better flavor and color. Glycerin is used extensively also in icings of various types to which it imparts softness and a smooth and glossy appearance, preventing at the same time the development of a brittle and crumbly character. The subject of the use of glycerin in bakery production and in food processing in general has been recently reviewed by Leffingwell and Lesser (27).

CHAPTER III

THE PROTEINS

General. Proteins are highly complex nitrogenous substances of primary importance, being present in all cells of plants and animals. They are originally produced by plants only, being synthesized from simple inorganic nitrogenous matter, various salts and water, the energy for this synthesis being supplied by sunlight. Animals are unable to accomplish such a fundamental synthesis and must ultimately rely for their protein needs upon the preformed plant proteins.

Chemically, the proteins consist of 50 to 55 percent of carbon, 25-30 percent of oxygen, 15 to 19 percent nitrogen, about 7 percent of hydrogen, 0.5 to 2.5 percent sulfur, and sometimes phosphorus and halogen. Such an elementary analysis, however, gives little indication of the complexity of the structure of proteins. It is only when proteins are split by hydrolytic agents into their component units that an idea of their highly ramified structure is obtained.

When a typical protein is exposed to the hydrolytic action of acids, alkalis or enzymes under suitable conditions, a mixture consisting entirely of alpha-amino acids is obtained. This fact has led to the conclusion that the protein molecule consists of a large number of different amino acids linked together into a long chain, analogous to the glucosidic chains of starch molecules. The amino acids thus form the basic structural units of protein complexes, just as the glucose units do in the case of the complex carbohydrates.

AMINO ACIDS

Alpha-amino acids are organic acids which contain an amino group (NH_2) attached to the alpha-carbon, that is, the first carbon atom following the carboxyl group (COOH), the second characteristic group. Their general formula may be written as follows:

$$\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{R.C}}-COOH$$
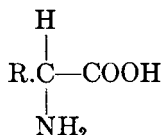
in which R may be any of a series of different groupings. The presence of the carboxyl group gives the amino acid its acidic properties, while the presence of the amino group imparts to it the properties of a base. It can therefore combine with either acids or bases and this amphoteric character accounts for the ability of amino acids to combine with each

other by means of the so-called peptide linkage (CO—NH) involving the two oppositely reactive groups.

While amino acids in general possess certain similarities in their properties attributable to their common possession of the carboxyl and amino groups, they differ markedly in individual characteristics due to the difference in the additional group attached to the alpha-carbon atom. This grouping ranges in complexity from a single hydrogen atom, as in the amino acid glycine, to a double cyclic group as in the amino acid thyroxine.

While several different systems for the classification of amino acids have been suggested, the one generally followed involves their division according to their reaction, that is, whether they are neutral, acidic or basic, and the presence of sulfur and of halogens in their composition. Neutral amino acids contain one amino and one carboxyl group and are hence also referred to as monoamino-monocarboxylic acids. They constitute the major portion of most proteins. Acidic amino acids contain one amino group and two carboxyl groups and are also known as monoamino-dicarboxylic acids. The predominance of the acidic group imparts to them the properties of a weak acid. Basic amino acids contain one carboxyl group and either two amino groups, when they are known as diamino-monocarboxylic acids, or one amino group and another complex basic group, when they are referred to either as homocyclic or heterocyclic acids. There are three sulfur-containing and two halogen-containing amino acids. More than twenty amino acids and closely related compounds have thus far been accepted as occurring naturally in proteins and their chemical constitution determined. The following table lists these amino acids, giving their chemical structure. It will be observed that they all contain the grouping $—CH(NH_2) \cdot COOH$, and that their structural difference is due to the variations of the additional grouping attached to the alpha-carbon atom.

TABLE 11. CHEMICAL STRUCTURE OF THE AMINO ACIDS

---

1. Monoamino-monocarboxylic Acids

Glycine, $CH_2(NH_2) \cdot COOH$

Alanine, $CH_3 \cdot CH(NH_2) \cdot COOH$

Valine, $(CH_3)_2.CH \cdot CH(NH_2) \cdot COOH$

Leucine, $(CH_3)_2.CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Isoleucine, $CH_3 \cdot CH_2$

$$CH_3 \cdot CH_2 \diagdown CH \cdot CH(NH_2) \cdot COOH \diagup CH_3$$

Norleucine, $CH_3 \cdot CH_2CH_2CH_2 \cdot CH(NH_2) \cdot COOH$

Serine, $CH_2(OH) \cdot CH(NH_2) \cdot COOH$

Threonine, $CH_3CH(OH) \cdot CH(NH_2) \cdot COOH$

2. Monoamino-dicarboxylic Acids

Aspartic Acid, $COOH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Glutamic Acid, $COOH \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Hydroxyglutamic Acid, $COOH \cdot CH_2 \cdot CHOH \cdot CH(NH_2) \cdot COOH$

3. Diamino-monocarboxylic Acids

Arginine, NH

$$C \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$$

$$NH_2$$
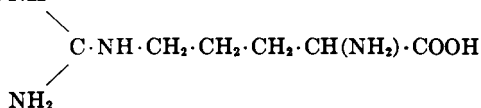
Citrulline, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Lysine, $CH_2(NH_2) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

4. Sulfur-containing Acids

Cystine, $S \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
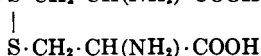
$$S \cdot CH_2 \cdot CH(NH_2) \cdot COOH$$

Cysteine, $HS \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Methionine, $CH_3 \cdot S \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

5. Homocyclic Acids

Phenylalanine, $C_6H_5CH_2 \cdot CH(NH_2) \cdot COOH$

Tyrosine, $C_6H_4OH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

Iodogorgoic Acid,
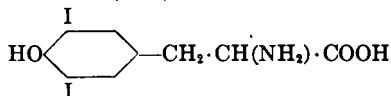
Thyroxine,
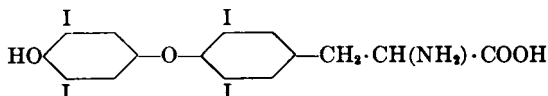
6. Heterocyclic Acids

Tryptophane,
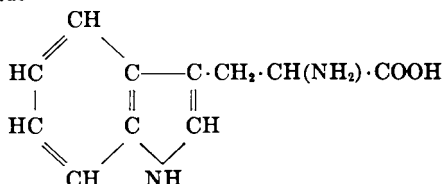
Histidine, $HC = C \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
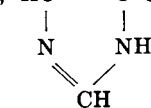
Proline, $H_2C - CH_2$
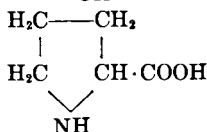
Hydroxyproline, $HOHC - CH_2$
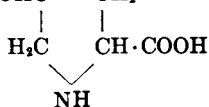
Amino acids, as previously indicated, constitute the building blocks of proteins. When protein foods are ingested by an animal organism, they are first enzymatically hydrolyzed into their constituent amino acids from which the organism then resynthesizes the specific types of proteins it requires for growth and bodily maintenance. The natural distribution of amino acids is by no means uniform among all proteins, many of the latter substances lacking one or more of the accepted amino acids in their make-up. It is therefore obvious that not all proteins are of equal nutritional value. Recent studies have shown that there are some ten amino acids which are indispensable to the animal organism if it is to grow or maintain itself. A protein lacking in any of these amino acids will therefore be deficient as a nutrient. The following table classifies the amino acids with respect to their effect upon growth.

TABLE 12.   CLASSIFICATION OF AMINO ACIDS WITH
RESPECT TO THEIR GROWTH EFFECT
(W. C. Rose. *Physiol. Rev. 18*, 109 (1938))

Indispensable	*Dispensable*
Lysine	Glycine
Tryptophane	Alanine
Histidine	Serine
Phenylalanine	Norleucine
Leucine	Aspartic Acid
Isoleucine	Glutamic Acid
Threonine	Hydroxyglutamic Acid
Methionine	Proline
Valine	Hydroxyproline
Arginine*	Citrulline
	Tyrosine
	Cystine

* Arginine can be synthesized by the animal organism, but not at a sufficiently rapid rate to meet the demands of normal growth.

TYPES OF PROTEINS

The innumerable proteins that occur in nature may be classified according to two broad systems. The first, so-called biological system groups the proteins according to their origin into plant proteins and animal proteins. The second, more generally used system classifies the proteins according to their general chemical nature into (1) simple proteins, (2) conjugated proteins formed by the association of a simple protein with some other group, and (3) derived proteins which are degradation products obtained by the hydrolytic breakdown of proteins. Each of these main groups is further subdivided, the first according to the solubilities of its members in various solvents, the second according to the nature of the associated non-protein group, and the third according to the degree of degradation. The following table gives the chemical

classification of the proteins as adopted by the American Physiological Society as far back as 1908 and which is still generally followed at present.

TABLE 13. CHEMICAL CLASSIFICATION OF PROTEINS
(American Physiological Society)

I. SIMPLE PROTEINS—Substances that yield only alpha-amino acids or their derivatives on hydrolysis

(a) Albumins—soluble in water or dilute salt solutions and coagulable by heat

Ovalbumin........................from egg white
Serum albumin................... " blood serum
Lactalbumin..................... " milk
Vegetable albumin............... " plant tissues

(b) Globulins—insoluble in water, soluble in salt solutions, and coagulated by heat

Ovoglobulin......................from eggs
Serum globulin.................. " blood serum
Edestin......................... " hemp seed
Amandin......................... " fruit kernels

(c) Glutelins—insoluble in neutral solvents, soluble in dilute acids or bases, and coagulable by heat; present in cereal seeds only

Glutenin........................from wheat

(d) Gliadins (or Prolamins)—soluble in 80 percent alcohol, insoluble in water, absolute alcohol, or neutral solvents; present in cereal seeds only

Zein............................from corn
Gliadin......................... " wheat
Hordein......................... " rye

(e) Albuminoids—insoluble in all neutral solvents

Elastin.........................from ligament
Collagen........................ " tendon
Keratin......................... " horn and hoofs

(f) Histones—soluble in water or dilute acids, precipitated by ammonia, not coagulated by heat; present in animal cells only

(g) Protamines—soluble in water, uncoagulable by heat. Simplest proteins or polypeptides, present in ripe generative cells only

II. CONJUGATED PROTEINS—Substances that consist of protein combined with some other substance (the prosthetic group or molecule)

(a) Nucleoproteins—compounds of one or more proteins with a nucleic acid

(b) Glycoproteins—compounds of protein with carbohydrates

(c) Phosphoproteins—compounds of proteins with a phosphorus compound other than lecithin or nucleic acid

Casein..........................from milk
Ovovitellins.................... " egg yolk

(d) Chromoproteins (Hemoglobins)—compounds of proteins with a chromophoric group

Hemoglobin......................from mammalian blood
Hemocyanins..................... " invertebrate blood
Chlorophylls.................... " green plants

(e) Lecithoproteins—compounds of proteins with lecithins

(f) Lipoproteins—compounds of proteins with fatty acids

TABLE 13. CHEMICAL CLASSIFICATION OF PROTEINS—*Continued*

III. DERIVED PROTEINS—primary and secondary degradation products of proteins

    (a) Metaproteins—products resulting from the action of acids or bases

    (b) Proteoses—products resulting from further hydrolysis. Soluble in water, and
            not coagulated by heat, precipitated by saturating their solutions
            with ammonium or zinc sulfate

    (c) Peptones—soluble in water, non-coagulable by heat, not precipitated by satu-
            rating their solutions with ammonium sulfate

    (d) Peptides—compounds of two or more amino acids possessing one or more
            —CO.NH— or peptide groups

I. The Simple Proteins.

The simple proteins are those which yield only alpha-amino acids and closely related compounds upon complete hydrolysis. Their classification by solubility reflects to some extent their molecular constitution since proteins in which the acidic group predominates are more soluble in bases than in acids and vice versa. Each individual protein's solubility is at a minimum at a certain pH which, in aqueous solutions free from neutral salts, coincides with the iso-electric point at which the electric charges of the molecule are exactly equalized. With most proteins this iso-electric point is in the pH range of 5 to 7. Proteins with a marked basic reaction are the protamines and histones which contain a high proportion of basic amino acids in their make-up. The most acid protein thus far isolated is the enzyme pepsin, which appears to be a globulin. Protein solubility also appears to be influenced by the molecular arrangement of the constituent amino acid units.

    (a) *The Albumins.*—The albumins, which occur in both animal and plant tissues, are characterized by the large number of amino acids which, in relatively small quantities each, make up their molecules, giving them an essentially neutral character since neither the basic nor the acidic amino acids predominate. Perhaps their outstanding character is that they are coagulated by heat and by strong alcohol. Typical animal albumins are lactalbumin from milk, ovalbumin from egg white and serum albumin from blood serum, while representative vegetable albumins are leucosin from wheat and legumelin from peas. The albumins are soluble in acids, alkalis, dilute salt solutions and distilled water. In more concentrated salt solutions the albumins are precipitated or "salted out" of solution.

    (b) *The Globulins* are similar in their distribution to the albumins, occurring in both animal and plant tissues. They are also characterized by the fact that their molecules consist of a large number of amino acids present in small quantities each. Finally, they also are subject to coagulation by heat and strong alcohol. Two types of globulins are dis-

tinguished, one type containing phosphorus and being insoluble in pure water, the other lacking phosphorus and being soluble in pure water. Globulins in general are more easily salted out than albumins. Representative animal globulins are lactoglobulin from milk and ovoglobulin from egg white. The plant globulins include such proteins as edestin present in hemp seed, wheat, oat, corn, etc., legumin from peas, and glycinin from soya bean.

(c) *The Glutelins.*—The glutelins are found only in grains in which they are always associated with the gliadins. A typical example of this protein is glutenin of wheat which is insoluble in water, salt solutions and alcohol, but readily soluble in dilute alkalis. Glutenin, in combination with gliadin and other wheat proteins, forms the all important dough gluten which will be discussed later in more detail.

(d) *The Gliadins.*—The gliadins, also known as prolamins, are found only in cereals, like the glutelins. Typical members of this group of proteins are gliadin of wheat, zein of corn and hordein of barley. When decomposed, they yield mainly glutamic acid, proline and ammonia, with very small quantities of basic amino acids. Zein is completely lacking in lysine and tryptophane, two indispensable amino acids, which greatly impairs its nutritional value. Gliadin is the second important constituent of dough gluten about which more will be said later. It is insoluble in water, but soluble in dilute acids and alkalis. It is also soluble in strong alcohol (70 to 90 percent) and differs in this respect from all other proteins.

(e) *The Albuminoids.*—The albuminoids, also called scleroproteins, constitute the connective tissue proteins of animals. They are subdivided into (a) the collagens which form the main constituent of animal tendons and which, upon careful hydrolysis, are converted into gelatin; (b) the elastin which predominates in filaments and consists chiefly of the amino acids glycine and leucine; and (c) the keratins which are the proteins forming the other protective tissues of the skin and such organs as hair, feathers, wool, hoofs and horns.

(f) *The Histones.*—This group of proteins is present in animal cells only where it usually occurs in combination with other substances, such as nucleic acid and iron compounds to form nucleoproteins and hemoglobins, respectively. They are slightly basic in reaction and are readily soluble in dilute acids. They form the main constituent of the red coloring substance of blood.

(g) *The Protamins.*—These proteins, which occur in both animal and vegetable cells, are composed almost entirely of basic amino acids which impart to them a strongly basic character. They occur mainly in the protoplasm of germ cells.

II. Conjugated Proteins

(a) *Nucleoproteins.*—The proteins of this group derive their name from the fact that they comprise the most important protein constituent of the cell nucleus which governs cell activity. They represent combinations of a protein with a complex phosphorus-containing substance called nucleid acid and are present in both animal and vegetable cells. The protein portion of nucleoproteins is either a histone or a protamine, both of which are basic proteins and are thus capable of combining with acids. Nucleoproteins of animal origin differ from those of plant origin in that the nucleic acids derived from these two respective sources differ in their constitution.

(b) *Glycoproteins.*—The glycoproteins constitute combinations of a protein with a complex carbohydrate. Representative members of this group are the mucins, which occur in the slimy secretions of animals, and the mucoids, which are rather viscous compounds widely distributed in cartilage and tendons.

(c) *The Phosphoproteins.*—These are animal proteins—representative members being casein from milk and ovovitellin from egg yolk—in which a protein is united with organic phosphorus. Casein, when acted upon by the enzyme rennin, forms an insoluble clot. The phosphoproteins are not coagulated by heat as are the albumins and globulins.

(d) *Chromoproteins.*—These proteins, of which hemoglobin is an important representative, are found in the blood of nearly all animals where they participate in respiratory reactions. Hemoglobin itself is a combination of globin, which belongs to the histones, with hematin, an iron-containing pigment. The chlorophylls of green plants also belong to this group of proteins.

(e) *Lecithoproteins.*—These are compounds in which protein is combined with lecithin, a phosphatide. They differ from phosphoproteins in that the phosphorus is present as an integral part of the lecithin molecule, and does not appear as such upon hydrolysis, whereas in the phosphoproteins the phosphorus becomes part of the protein molecule from which it may be split off in the form of inorganic phosphorus.

III. Derived Proteins.

These substances are products obtained by the partial degradation of natural proteins either by enzymes or by other suitable agents, such as acids, alkalis, heat, etc. They are classified on the basis of their decreasing complexity into metaproteins, proteoses, peptones and peptides. This classification also coincides with the gradual loss of colloidal characters. The *metaproteins* are the first products obtained by protein hydrolysis. They are insoluble in water, but are soluble in dilute acids and alkalis

and are not coagulated by heat. The *proteoses* are unique among proteins and protein derivatives in that their precipitate formed by the action of nitric acid dissolves when the liquid is heated and reappears when the liquid is cooled. The *peptones*, products of still simpler constitution, are practically devoid of colloidal properties and are readily diffusible through semi-permeable membranes. They are distinguished from proteoses chiefly by differences in their precipitability. Mixtures of these two protein derivatives are relatively difficult to separate. The *peptides* are substances whose composition is known. They are formed by the condensation of two or more amino acids by means of a peptide link. Depending upon the number of amino acid units which enter into their formation, they are differentiated into dipeptides, tripeptides, tetrapeptides, etc., with the higher members known as polypeptides. A number of peptides have been synthesized in the laboratory from free amino acids. Glutathione, a compound present in yeast, wheat germ and many animal tissues, is a member of the peptide group.

STRUCTURE OF PROTEINS

The protein molecule has been found to consist of a large number of a limited variety of amino acids linked together by the so-called peptide linkage. This linkage is formed by the interaction of the hydroxyl group and the amino group, respectively, of two amino acids, with the elimination of one molecule of water. This chemical condensation reaction may be represented as follows:

$$CH_2{-}C{=}O + CH_2{-}C{=}O \xrightarrow{-H_2O} CH_2{-}C{=}O \qquad CH_2{-}C{=}O$$

(structure with NH₂, OH, H, NH, OH below; glycylglycine dipeptide with central N—H)

Glycine	Glycine	Glycylglycine (a dipeptide)
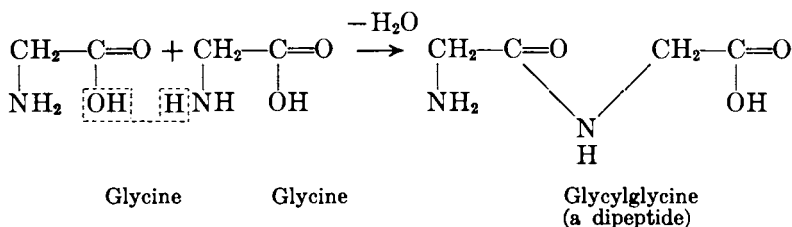
Since, as is apparent from the above reaction, the amino acids each lose at least either an H or an OH when they combine, the remaining units are referred to as amino acid residues. A very large number of such units may thus combine to form a long polypeptide chain of the following general order:
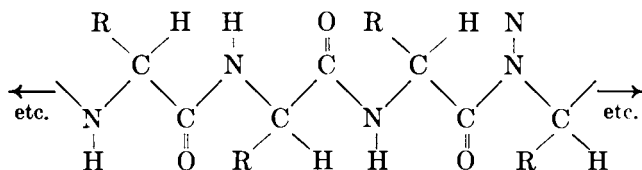
From this structural formula it is apparent that if a long polypeptide chain is fully extended, its backbone, consisting alternately of one nitrogen atom and two carbon atoms, assumes a zigzag structure, with the R groups projecting as side chains alternately above and below the plane of the backbone (*28*). The differences in chemical properties of the various proteins are due to the side chains which, as has been pointed out previously, may range in complexity from a single hydrogen atom to straight, branched or cyclic groups. As Lloyd and Shore state (*28*), "The electrical charge on the protein molecule, the polar character, the physical properties, the chemical activities, the capacity for hydration are all largely determined by the side chains."

The peptide linkage theory, proposed by Emil Fischer, is now generally accepted as affording a satisfactory explanation of the manner in which the amino acid residues are united in a protein chain. However, not all observable properties of proteins can be fully accounted for by such a peptide chain and a number of modifications of this concept have been proposed. These modifications on the whole are attempts to explain the globular and crystalline structures of proteins without doing violence to the peptide theory.

Very briefly considered, most of these newer concepts hold that the long polypeptide chains of proteins do not remain straight but, being flexible, tend to fold into semi-cyclic or cyclic forms, this condensation of the chains being promoted by the cohesion forces which attract the various parts of the chain to each other. Two of the suggested forms are shown in the figures on the opposite page of which the first indicates a semi-cyclic form as formulated by Astbury (*29*), and the second a cyclic form proposed by Wrinch (*30*).

If it is considered that the amino acids represented in a polypeptide chain may vary considerably and that furthermore they may combine in a great variety of sequential arrangements, an idea is obtained of the tremendous complexity of the protein molecules to which they give rise. From various investigations it would appear that the various amino acid residues are not distributed at random in a polypeptide chain but occur at constant intervals; i.e., each amino acid residue recurs with a characteristic whole number frequency. This concept of periodicity, applied to a protein like egg albumin, works out something like this: glutamic acid occurs with a frequency of 1 in 8; aspartic acid, 1 in 18, methionine, lysine and arginine, 1 in 24; tyrosine, 1 in 36, and histidine and cysteine, 1 in 72. Since the smallest number that accommodates these ratios is 288, the molecule of egg albumin must contain either 288 residues or a multiple thereof. If one molecule consists of 288 residues, then its molecular weight would be the average residue weight multiplied by 288.

$$
\begin{array}{ccccccccc}
& \text{NH—CO} & & & \text{NH—CO} & & & \text{NH—CO} & \\
\text{RHC} & & \text{CHR} & \text{RHC} & & \text{CHR} & \text{RHC} & & \text{CHR} \\
\text{CO} & \text{HN} & & \text{CO} & \text{HN} & & \text{CO} & \text{NH} & \\
\text{CO—CHR—NH} & & & \text{CO—CHR—NH} & & & \text{NH} &
\end{array}
$$

Folded Polypeptide Chain
(Astbury)

$$
\begin{array}{ccc}
& \text{CO—NH} & \\
\text{RCH} & & \text{CHR} \\
& \text{N—C} & \\
\text{RCH—C(OH)} & & \text{N—CHR} \\
\text{NH} & \text{N—C(OH)} & \text{CO} \\
\text{CO—CHR} & & \text{RCH—NH}
\end{array}
$$

Cyclic Polypeptide
(Wrinch)
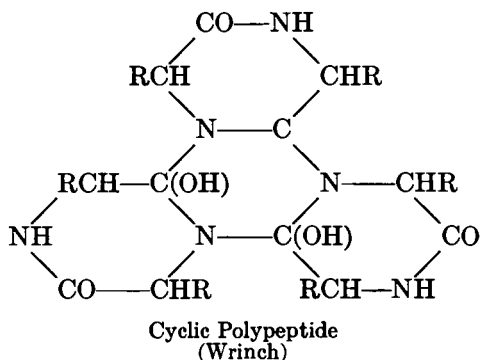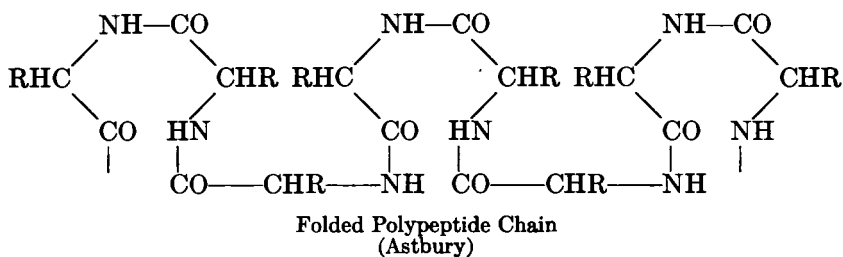
In the case of egg albumin the average calculated residue weight approaches 124 which would give a value of 35,700 as the molecular weight. This value agrees closely enough with values obtained for egg albumin by the ultra-centrifuge method, which range between 34,000 and 36,000, to justify the conclusion that there are 288 amino acid residues in one molecule of egg albumin. Proteins are thus seen to be compounds of very high molecular weights. These molecular weights, which in the case of hemocyanins run to several millions, have been shown to be multiples of two fundamental weights, namely 35,000 and 400,000.

These various theories or postulates afford an explanation of the different forms in which proteins are encountered in nature. Thus if the backbones of polypeptide chains are joined end to end, a fibrous structure results. If they are joined parallel to each other, a laminar structure is obtained. If the chains fold or coil into so-called piles, or assume cyclic forms, globular structures are formed. "Thus the fibrous molecules, or one dimensional, build the laminary or two dimensional and these in turn the globular. The fibrous may also form the globular directly by coiling" (*31*).

Evidence obtained mainly by the use of the ultra-centrifuge and X-ray investigations indicates that there is some fundamentally stable configuration of the protein molecule corresponding to a globular form and to a molecular weight which approximates 35,000 or a multiple of that figure,

excepting the hemocyanins in which the basic molecular weight approximates 400,000. A protein molecule in solution is a rather large object when compared with the surrounding water molecules. While protein molecules will not separate from aqueous solution under ordinary conditions, they may be made to settle out or sediment when a strong centrifugal force, such as is obtained with high-speed centrifuges, is applied to them. Svedberg and his co-workers (32) have made use of this fact in studying the properties of proteins in solution. They have found that most proteins form so-called "homodispersed" solutions, i.e., solutions in which the individual particles are of uniform size, either in the spherical form or approaching the spherical. These particles are to be considered as the actual protein molecules. The radii of these spherical molecules range from 2.2 mμ up to 12 mμ (33). Proteins with a molecular weight of 35,000 or a multiple have a radius between 2 and 4 mμ, examples being 2.17 mμ for ovalbumin and 3.9 mμ for edestin, while those with a molecular weight of 400,000 or a multiple have a radius of 12 mμ and upwards.

PROPERTIES OF PROTEINS

Protein Coagulation and Denaturation. When protein in solution is boiled, a precipitate is formed which does not redissolve when the solution is cooled. The insoluble substance is coagulated protein, differing in several important respects from soluble native protein. Although not all proteins are heat-coagulable, this loss of solubility is a unique property of most proteins and may be used as a means for separating proteins from non-protein material. Coagulation by heat occurs only in the presence of water. When carefully dried native protein is exposed to boiling temperatures, it will retain its solubility. Thus crystals of egg albumin, dried at moderate temperature, were heated to 120° C. (248° F.) in a current of dry air without loss of solubility. When steam at 120° C. was used, they became insoluble in five minutes (28).

Heat coagulation consists of two distinct reactions. The protein is first changed into a form which is insoluble at the isoelectric point. This change is called denaturation. The second reaction is the precipitation of the heat denatured protein at its isoelectric point. The existence of these two phases of coagulation may be shown by heating protein in an acid solution. Here denaturation occurs, but the denatured protein is kept in solution by the acid. If, however, the acid is neutralized, precipitation occurs rapidly. Heat-coagulated protein is dissolved also if sufficient alkali, urea, or a salicylate is added, and is re-precipitated upon neutralization or removal of the added substances. In addition to heat, protein denaturation can also be produced by acids, alkalis, salts of heavy

metals, alcohol, acetone, and such physical means as pressure, ultra-violet light, adsorption, shaking, etc. "If a solution of egg albumin is shaken with air, insoluble protein is formed which has the general properties of heat-coagulated protein. The first step in coagulation by shaking is the spreading of the protein at the air-water surface to form a monolayer. Whereas egg albumin in solution is a globular protein, the protein in the surface monolayer has been opened and its thickness is that of a single polypeptide chain" (*34*). Many of the changes which occur upon the mechanical mixing of dough and during fermentation are attributable to some forms of denaturation of the gluten proteins.

Denatured proteins differ from native proteins in several important respects. Very briefly summarized, these differences include the appearance of reactive —SH and —S—S groups, an uncoiling of the globular configuration into straight chain proteins, an inactivation in the case of enzymes which are of a protein nature, an increase in the digestibility of many proteins, loss of crystallizability, increase in viscosity, and others (*34*). Denaturation, formerly thought to be completely irreversible, has more recently been shown to be reversible in the case of several proteins.

Protein Films. Many proteins can be induced to spread in a monomolecular layer or film on water. They derive this property from the fact that their molecules consist of polar or water attracting and nonpolar or water non-attracting parts. "It should be noted that if the ratio of water attracting to water non-attracting groups be high, the molecules as a whole will be dragged into the solvent and hence no film will be formed since the substance will dissolve. If the ratio be low no film will be formed since the substance will remain as a separate phase on the surface of the water: pure hydrocarbon oils, for instance, do not spread, but remain as globules on water" (*28*). Among proteins, gelatin is too soluble to form a film, while fibrinogen and myosin do not form a film readily because they are not soluble enough.

Maximum film formation occurs at the iso-electric point of the protein and is reduced on either side of the iso-electric point. The extreme thinness of protein films is indicated by the fact that 1 mg. of protein will spread over 1 square meter of surface. "The volume of the molecule may be as great as 44,000 cubic Ångströms, but the thickness is from 6 to 7.5 Ångströms" (*28*) (1 Ångström unit equals 0.1 mμ.) Since most proteins in solution occur in the globular form, film formation constitutes a denaturation since there is evidently an unfolding of the molecule as it passes into the surface film. This denaturation has been shown to be reversible in the case of several proteins. According to Hughes and Rideal (*35*) each molecule in a fully extended protein film occupies its own area of surface with both the backbone and side chains lying flat

on the surface. In compressed films the molecules have turned so that the side chains are submerged and only the backbones lie flat on the surface.

Protein Swelling. Katz (*36*) in defining the phenomenon of swelling, laid down three criteria as characterizing real swelling: "A solid is said to swell when it takes up a liquid, whilst at the same time, (a) it does not lose its apparent (microscopic) homogeneity; (b) its dimensions are enlarged; (c) its cohesion is diminished; instead of hard and brittle, it becomes soft and flexible."

He further distinguished between three types of swelling, which he called intermicellar, intramicellar, and permutoid types of swelling. They differ primarily in the degree of penetration of the liquid between and into the molecular particles. In intermicellar swelling, the liquid penetrates merely between the micelles or protein particles. In intramicellar swelling, the liquid penetrates into the interior of the structure of protein molecules. In permutoid swelling, there is an interaction of the liquid and the solid to form a loosely combined chemical compound.

Certain substances capable of swelling will take up only a certain amount of liquid and no more. Most protein gels behave in this manner. Such substances are said to exhibit what is called a limited swelling and a swelling maximum. Some proteins, however, such as egg albumin, swell without limit, becoming eventually liquefied and finally go into solution. Such substances are said to exhibit unlimited swelling. "There is no sharp dividing line between substances which show a swelling maximum and those that undergo unlimited swelling. The same substance under one set of conditions may show a maximum of swelling and under another set of conditions unlimited swelling" (*37*). The transition from the condition of swelling to that of solution generally occurs in imperceptible degrees in the case of proteins exhibiting unlimited swelling.

When gluten is washed from flour dough it will contain approximately two-thirds water in its wet state and gluten thus exhibits a swelling maximum. Gortner and Doherty (*38*) studied the rate of swelling of gluten from strong and weak flours in various dilute acids and found the rate to be greater for strong flour glutens than for weak flour glutens. This led them to the conclusion that "the difference between a strong and a weak gluten is apparently that between a nearly perfect colloidal gel with highly pronounced physico-chemical properties and that of a colloidal gel in which these properties are less marked." In other words, strong glutens possess a superior structure as compared with weak glutens. The structural characteristics of a gluten are determined primarily by wheat variety and secondarily by environmental conditions during growth, wheat maturation and storage. Adverse environmental factors

will generally damage the inherent superiority of a gluten. Thus a wheat possessing originally a strong gluten, as distinguished from high protein content, may be rendered unsatisfactory for baking purposes by prolonged storage at high temperatures and under damp conditions.

European cereal chemists and baking technologists make rather extensive use of the capacity of gluten to swell in dilute acids as a means of determining flour quality. Application of methods developed on this principle have shown that a satisfactory correlation exists between the swelling number of gluten and the loaf volume obtained from the corresponding flour. Since the swelling number is a measure of gluten quality only, the protein content of the flour must also be taken into consideration in predicting flour behavior as protein content exerts an effect of its own on ultimate loaf volume.

THE PROTEINS OF WHEAT

Wheat is unique among all other cereals in that its milled product, flour, is alone capable of forming a dough that will retain the gas evolved during fermentation and upon baking yield a light well-aerated bread. This unique characteristic is imparted to wheat by its proteins which, on combining with water, result in the gluten, the actual substance that confers on dough the property of gas retention. Because of the preeminent position which the wheat proteins occupy in baking it is not surprising that a great amount of research has been expended on them, and it is indicative of the complexity of protein material in general that many basic questions still remain to be answered. While protein was first suspected as the quality determining factor of wheat flour as far back as 1728, its first systematic study was not undertaken until the turn of the present century when Osborne and his associates published a classic report on their work with the proteins of the wheat kernel. Since that time, numerous workers have devoted their main labors to an elucidation of the many problems associated with the composition and functions in dough formation and development of wheat proteins. The remaining portion of this chapter will summarize as briefly as possible some of the major findings in this field.

When flour and water are mixed into dough and this is kneaded thoroughly under water either by hand or by machine, a coherent, extensible, and rubbery mass is obtained consisting principally of protein and water. This so-called "crude gluten" contains about 65 to 70 percent water, while its solid matter, or dry substance, usually contains 75-80 percent protein, 5-15 percent starch which failed to wash out, 5-10 percent lipids, and small quantities of mineral salts. The gross compositions of two samples of dry crude gluten are given in the following table cited by Blish, (*39*)

which indicates rather clearly that crude glutens exhibit a wide range of variations as to content of total protein, carbohydrates, lipids and ash.

TABLE 14.   COMPOSITION OF DRY CRUDE GLUTEN

	Gluten A (soft wheat)	Gluten B (commercial product)
	percent	percent
Protein (N × 5.7).....................	72.7	81.0
Lipids (neutral extraction method)........	7.1	11.6
Ash..................................	0.6	0.9
Carbohydrates........................	18.8	4.9

Osborne (40) had concluded from his extensive studies that the gluten constituted some 80 percent of the total wheat flour protein and that the proteins of the gluten consisted of two distinct individual proteins, glutenin and gliadin, which are present in nearly equal amounts. The non-gluten proteins, amounting to about one-fifth of the total flour protein, he identified as leucosin, which is an albumin, edestin, which is a globulin, and a small quantity of proteose which is classed among the derived proteins. These non-gluten proteins, which are soluble either in water or dilute salt solutions, are presumably nonessential to the formation of gluten and are largely removed in the gluten washing process.

When crude gluten is treated with 70 percent alcohol, the gliadin fraction dissolves or disperses and can be obtained in fairly pure form. The remainder of the protein consists essentially of glutenin which is soluble in dilute acid or alkali solutions. The use of alcohol in gliadin extraction has a pronounced denaturing effect upon the glutenin fraction which, as a consequence, becomes strongly resistant to practically all solvents except caustic alkali. Glutenin dispersed by dilute alkali is irreversibly changed in its physical properties and is no longer identical with the substance as originally present in gluten.

Considerable doubt has in recent years been cast upon the former concept that both gliadin and glutenin form homogeneous protein aggregations. For example, when applying ultra-centrifugal, electrophoretic, diffusion or related techniques to the more easily dispersible gliadin fraction, it has as yet proven impossible to establish the homogeneity of presumably pure gliadin preparations. Studies of gluten dissolved in salicylate solution have led to the conclusion that gluten consists of a protein system of many components varying progressively in solubility and other physical properties rather than of only two or three distinct protein components. Molecular weight determinations have resulted in estimates ranging from 15,500 to 125,000 for gliadin and of 36,400 for

glutenin. Even though the validity of Osborne's original designation of gluten as an intimate mixture of only two proteins is no longer acceptable, it is nonetheless desirable to retain the terms gliadin and glutenin in referring to these two types of protein, at least until their true character has been established.

When gluten is separated by conventional methods into its two main constituents, and these are subjected to an elementary analysis, values are obtained which agree well with the original analytical findings of Osborne, given in the following table.

TABLE 15. ELEMENTARY ANALYSIS OF GLIADIN AND GLUTENIN
(Osborne)

	Gliadin Percent	Glutenin Percent
Carbon.........................	52.72	52.34
Hydrogen.......................	6.86	6.83
Nitrogen.......................	17.66	17.49
Oxygen.........................	21.73	22.26
Sulfur.........................	1.03	1.08

It will be seen that these two types of proteins are very similar in elementary composition. It is also evident that because of the close agreement between the nitrogen values of the two proteins the use of the factor 5.7 for multiplying the total nitrogen as obtained by the Kjeldahl method will give a satisfactory approximation of the quantity of gluten protein in gluten or in various protein fractions prepared from it.

Since it was recognized that proteins are built up of amino acids, the whole gluten and purified samples of gliadin and glutenin have been subjected to many analyses to determine their amino acid composition. In Table 16 are given the amino acid compositions of gluten, gliadin and glutenin, respectively, as reported by Blish (*39*), whose following related comment will prove of interest: "The outstanding feature of gluten protein composition is the extraordinarily high content of glutamic acid, especially in gliadin, where glutamic acid constitutes nearly half of the entire protein substance. Noteworthy also are the large proline content and the relatively small amounts of basic amino acids and of tryptophane. The obvious lysine and tryptophane deficiencies indicate a limited nutritional value, an indication which has been abundantly confirmed experimentally."

Ever since it was established that gluten formed the principal quality determining substance of flour numerous attempts have been made to correlate the baking quality of a flour with the proportions in which glutenin and gliadin were present. It was originally thought that since these two types of proteins differed in their physical properties, their

TABLE 16.   AMINO ACID COMPOSITION OF GLUTEN PROTEINS

	Gluten	Gliadin	Glutenin
	Percent	Percent	Percent
Arginine........................	4.3	3.2	4.7
Lysine.........................	2.1	0.6	1.9
Histidine.......................	2.4	2.1	1.8
Tyrosine.......................	4.2	3.1	5.1
Tryptophane....................	1.1	0.9	1.8
Phenylalanine...................	2.0	2.5	2.0
Cystine........................	1.9	2.3	1.7
Methionine.....................	3.3	2.3	—
Serine.........................	—	0.1	0.7
Threonine......................	2.5	3.0	—
Leucine and Isoleucine............	6.0	6.0	6.0
Valine.........................	3.0	3.0	1.0
Glutamic acid...................	36.0	46.0	27.2
Aspartic acid...................	—	1.4	2.1
Glycine........................	—	1.0	1.0
Alanine........................	5.5	2.5	4.4
Proline........................	11.0	13.2	4.4
Hydroxyproline.................	—	—	—
Ammonia.......................	4.5	5.1	4.0

varying concentrations in different flours would exert a prominent effect upon the baking behavior of the flours.   Thus Snyder (41) working with hard wheats arrived at the conclusion that a gluten consisting of 65 percent gliadin and 35 percent glutenin possessed the best physical properties, while Fleurent (42), working with soft European wheats of low protein content believed the ratio of 75 percent gliadin to 25 percent glutenin to be the most desirable.   More recent work by Grewe and Bailey (43), however, indicates that there exists no consistent proportional relationship between the gliadin content of a flour and its baking quality as judged by its loaf volume.   These authors examined flours which ranged in gliadin content from 4.32 percent to 7.07 percent and gave loaf volumes ranging from 1,810 cc. to 2,200 cc.   The 2,200 cc. loaf volume was obtained from flour containing 5.35 percent gliadin, while a loaf volume of 2,020 cc. was obtained from flour containing 4.32 percent gliadin, thus indicating a rather poor correlation.   There is general evidence which suggests that the glutenins and the gliadins obtained from different wheats are identical in their chemical composition and configuration, that is, pure samples of glutenin obtained from different wheats will disclose the same amino acid composition and the same structural molecular arrangement, and the same holds true of pure samples of gliadin.   Differences in baking behavior of different flours cannot, therefore, be attributed to chemical differences in their respective glutenins or gliadins.   As Swan-

son (*31*) points out "Differences in baking behavior, as far as they are due to the proteins, are caused by the physical state rather than the chemical constitution."

Protein Content of Wheat. The amount of protein deposited in the wheat kernel, and to some extent also the characteristics of the protein, appear to be largely determined by environmental factors, such as soil, rainfall, temperature, etc. (*44, 45*). All proteins, as indicated previously, contain carbon, hydrogen, oxygen, and nitrogen. Some proteins also contain sulfur and phosphorus. The plant, in its synthesis of protein, derives these elements from the carbon dioxide of the air, and from the water, nitrogen compounds and mineral substances in the soil. Since the supply of carbon dioxide is for all practical purposes limitless, it is the soil constituents which form the chief limiting factors in protein production. Barmore (*45*) has summarized the effect of environment on wheat protein content as follows:

"The limiting factor in the production of protein appears to be in the amount of available nitrogen in the soil at different stages of development of the crop in relation to soil moisture, mineral nutrients in the soil, and environmental factors. Total rainfall, the seasonal distribution of rainfall, and the temperature have a profound effect on the amount of protein, and in some cases, on the characteristics of the protein produced. Differences in protein content among varieties of wheat grown under comparable conditions are very small as compared to differences due to soil and environment. It is unusual to find an average difference of one percent in the protein content even of hard and soft varieties grown under comparable conditions unless there is a big difference in their yield of grain."

Wheat varieties range in protein content from 6 to 18 percent, depending largely on the regional environments in which they are grown. High nitrogen soils characterize in general the hard wheat areas and account for the high protein grains, whereas the soils in soft wheat areas are usually much poorer in their amount of nitrogen compounds and thus produce grain low in protein content. Rainfall, both in its amount and distribution, exerts a considerable effect upon the protein content of wheat. Generally speaking, soils in areas of low rainfall are relatively high in organic matter, and therefore also in nitrogen compounds, compared to soil in areas of high rainfall. The result is that wheats originating in low rainfall areas will tend toward higher protein contents because of the greater nitrogen supply. Rainfall has also a more direct effect upon the protein content of wheat in that low rainfall will produce reduced yields of grain in which the available soil nitrogen will have been synthesized into a relatively larger proportion of protein in relation to the smaller grain volume.

Rain distribution during the growing season is also of importance since the wheat plant utilizes soil nitrogen not only during grain formation but also during its vegetative growth. High rainfall early in the season will promote vegetative growth so that more soil nitrogen is utilized before heading and blossoming with less being available for protein production in the grain. · Under such conditions the amount of nitrogen available during grain formation and maturation is limited and the protein content of the grain is reduced.

Temperature also influences protein deposition in the grain. "Relatively cool temperatures during the period of kernel growth promote the formation of carbohydrates, prolong the maturation process, and result in larger quantities of starch and consequent lower percentages of protein. Conversely, relatively high temperatures and lower soil moistures, which normally prevail in the Great Plains after crop has headed, tend to reduce carbohydrate synthesis and storage and to shorten the maturation period, resulting in a lower yield of grain of higher protein content" (*45*).

The annual fluctuations encountered in protein content of the wheat crop in any given area can thus be explained on the basis of fluctuations in the weather during the growing season. Weather conditions are never identical from year to year for any one area so that nitrification, the proportional use of available nitrogen in vegetative growth and maturation and the amount of carbohydrate synthesis are also never identical. The protein contents of wheats are to some extent affected even by such seemingly unimportant factors as the time of seedbed preparation and the type of tillage implement employed. Thus the protein content of wheats will vary from year to year for districts and regions and within the same year for different fields.

CHAPTER IV

ENZYMES

General. Enzymes are biological catalysts of a protein nature elaborated by living tissue. Catalysts are defined as substances which are capable of altering the rate of a reaction without undergoing a chemical change themselves. An enzyme conforms to the accepted definition of a catalyst in that (1) it increases the rate of a chemical reaction; (2) the increase is proportional to the concentration of enzyme present; (3) the enzyme does not itself form a part of the reaction products. To this may be added the further similarity between enzymes and inorganic catalysts that small amounts of either affect relatively large emounts of the material acted upon (substrate). On the other hand there are several marked differences. Enzymes are usually characterized by a well-defined specificity, and are sensitive to high temperatures. Enzymatically catalyzed reactions usually proceed at a much lower temperature than would otherwise be possible. For example, the conversion of starch to sugar in the laboratory requires extensive boiling of the starch suspension in the presence of acid, whereas in plants or animals the enzyme amylase converts starch into maltose at a temperature below 100° F.

Enzymes are named by adding the suffix "ase" to the name of the substrate they act upon. Thus the enzymes which convert amylose (starch) into simpler carbohydrates are called amylases, the one which acts upon maltose, maltase, etc. A number of enzymes were given names prior to the adoption of this system of nomenclature and some of the older designations have been retained. Examples are trypsin, pepsin and papain, three proteolytic enzymes capable of breaking up large protein molecules into smaller constituents. The term diastase for starch converting enzymes is slowly being replaced in the more recent literature by the term amylase.

Classification. Enzymes are classified into two major categories according to the type of reaction they catalyze. One such basic reaction involves the breaking up of larger compounds into simpler ones with the addition of water. This type of reaction is called hydrolysis and the enzymes catalyzing it are hydrolytic enzymes or hydrolases. The so-called desmolases and oxidases comprise the second group of enzymes which bring about transformations without addition of water or oxygen,

and which produce true rupture of molecules. The following table gives a partial list of representative enzymes classified according to this system.

TABLE 17. CLASSIFICATION OF ENZYMES

A. HYDROLASES

    (1) *Esterases*
        (a) Lipases—hydrolyze fats to glycerol and fatty acids
        (b) Phosphatases—act on phosphoric esters

    (2) *Carbohydrases*
        (a) Invertase—inverts sucrose to invert sugar
        (b) Maltase—hydrolyzes maltose to glucose
        (c) Lactase—transforms lactose to glucose and galactose
        (d) Amylases (Diastases)—convert starch to maltose
        (e) Emulsin—hydrolyzes beta-glucosides

    (3) *Proteases*
        (a) Pepsin—hydrolyzes proteins into simpler proteoses and peptones
        (b) Trypsin—hydrolyzes proteins to polypeptides and amino acids
        (c) Papain—hydrolyzes proteins to peptides
        (d) Rennet—hydrolyzes casein to paracasein

    (4) *Amidases*
        (a) Urease—changes urea into carbon dioxide and ammonia
        (b) Arginase—acts on arginine to produce urea and ornithine

B. OXIDASES

    (a) Catalase—changes hydrogen peroxide to oxygen and water
    (b) Zymase—ferments glucose to carbon dioxide and alcohol.

PROPERTIES OF ENZYMES

Before discussing in greater detail the enzymes of wheat flour and yeast which make possible the dough fermentation process, it might be well to indicate briefly some of the more prominent characteristics shared by most enzymes.

Enzymes in general show a pronounced specificity, that is, they are highly limited as to the nature of the reaction they catalyze. A good example of such specificity is the action of emulsin, an enzyme found in bitter almonds and other plant tissues, and of maltase present in malt, yeast, etc. Both of these enzymes hydrolyze or ferment glucosides, which are compounds of glucose chemically modified by the addition of a simple alcohol. However, while emulsin will act only on those glucosides which contain the beta structure, maltase hydrolyzes only an alpha-glucoside.

Enzymes are characteristically heat labile, or subject to inactivation by high temperatures. If heat is applied to an enzyme reaction, e.g., the conversion of starch to maltose by amylases, it will be found that the rate of reaction, initiated at room temperature, will increase rapidly as the temperature of the medium rises. Conversion to maltose is found

to proceed fastest within a temperature range of 38° and 55° C. (approx. 100° and 130° F.). A further rise in temperature results in a drop of maltose production, and conversion ceases almost completely after the temperature has exceeded 60° C. (140° F.). If the reaction medium is then permitted to cool to 38° C., no further starch conversion takes place. The amylases have been inactivated or destroyed and no longer possess any catalytic properties. A typical curve showing the effect of temperature upon maltose formation from starch by the action of amylase is reproduced in the following figure taken from the data by W. M. Sandstrom (46).

The temperature at which inactivation of a given enzyme occurs depends to a large extent upon such factors as time, hydrogen ion concentration, and moisture content. Taking the amylases again as an example, rapid inactivation is obtained at a temperature of 60° C. (140° F.) when the enzymes are present in an essentially liquid medium, such as a 2 percent soluble starch solution normally used in laboratory tests. However, these enzymes retain their activity up to 82° C. (approx. 180° F.) and higher in bread doughs during the first

Fig. 12—Effect of temperature upon the yield of maltose from starch by the action of malt diastase. (*Courtesy American Assoc. of Cereal Chemists.*)

stages of baking, since here the moisture content is considerably lower than in starch solutions. Enzymes will withstand short exposure to high temperatures without marked effect on their activity, but are greatly weakened by long exposures to medium high temperatures. The pH reaction, or hydrogen ion concentration, also affects to a considerable degree the resistance of enzymes to high temperatures. Temperature inactivation is brought about by a denaturation of the enzyme protein. This denaturation results in a drastic change of the protein structure, thereby destroying the activity of the enzyme.

The pH value, which is a measure of the acidity or alkalinity of the reaction medium, also exerts an important influence upon enzyme activity. Given otherwise specified conditions, each enzyme reacts most actively at a certain well-defined hydrogen ion concentration. This optimum pH value varies rather widely with different enzymes and with the

same enzyme when other conditions, such as temperature, concentration of substrate, or duration of reaction are changed. This is indicated by the following table by Hopkins, Cope and Green (*47*) which gives the percentage of maltose produced from 100 ml. of 2 percent soluble starch solution at various pH values by 1 ml. of a solution of precipitated barley amylase in 30 minutes at 37° C. (98.6° F.) and 58° C. (136.4° F.).

TABLE 18. INFLUENCE OF PH ON SACCHARI-
FICATION OF SOLUBLE STARCH BY BARLEY
AMYLASE

| | Percent Maltose Produced | |
pH	at 37° C	at 58° C.
3.7	27.65	2.60
4.2	46.90	14.24
4.67	47.50	19.30
5.4	44.60	18.87
6.2	42.35	12.85
7.1	42.15	9.25
7.8	35.10	0.86
8.2	27.90	0.30

The figures indicate that the pH optimum in these experiments was at 4.67 for both temperature levels. However, maltose production was considerably greater at the lower temperature. Furthermore, enzyme inactivation at the higher pH values was accentuated at the higher temperature. Obviously under these experimental conditions, a temperature of 136° F. was too high for optimum enzyme activity at any pH value.

Other factors influencing the rate of enzyme action are enzyme concentration, nature of the substrate, time or duration of reaction, and the presence of either activators or enzyme inhibitors.

The concentration of the enzyme is of importance since the rate of reaction depends largely upon the quantity of enzyme present and may under certain favorable conditions be directly proportional to it. Under most conditions, however, while higher enzyme concentrations do produce an increase in reaction velocity, this increase seldom approaches direct proportionality. Thus if the diastatic activity of one flour is twice that of another flour, as measured on a 2 percent soluble starch solution, this does not mean that during dough fermentation the first flour will yield twice as much maltose as will the second flour. There will be some increase in the first flour's maltose production, but it will not be directly proportional to its higher enzyme concentration as compared with the second flour.

That this should be so is not surprising if the nature of the substrate

is considered. Normally flour contains but a small amount of starch that is readily susceptible to enzyme attack. The rate of diastatic activity is, therefore, limited to a marked degree by the quantity of ruptured and hydrated starch granules, regardless of the relative amounts of amylases present, provided of course that a necessary minimum of enzyme is available. The nature or condition of the substrate is thus seen to be an important factor governing the rate of enzymic action.

The duration of the enzyme reaction is also of importance. If sufficient substrate is present and the enzyme is not otherwise inactivated, then the amount of change produced by an enzyme will be directly proportional to the time for which the reaction is permitted to proceed.

Certain enzymes cannot function in the absence of certain specific substances naturally associated with them and variously known as activators or coenzymes. As a rule the term coenzyme is applied to a substance which forms an essential part of an enzyme system without which enzymatic activity does not occur. Enzymes which consist of several distinct components are not uncommon, especially among the oxidizing and fermenting enzymes. In such systems, the entire enzyme is known as holoenzyme, the enzyme proper as the apoenzyme, and the dialyzable heat-stable fraction as the coenzyme. Harden and Young (48) were first to separate the heat-stable cozymase from the yeast enzyme zymase which brings about alcoholic fermentation. Neither this coenzyme nor the enzyme residue were able to produce alcoholic fermentation, but they regained the activity upon being recombined by mixing. Coenzymes are thus as important to enzyme activity as the apoenzymes since in their absence the entire enzyme system is inactivated.

Activators are substances which accelerate the velocity of an enzyme reaction, and may also extend the reaction of an enzyme to substances which it normally does not attack. The increase in rate may vary from a few to several hundred percent (46). A striking example of activation is that of papain which normally acts only on protein, but in the presence of hydrocyanic acid is able to attack peptones.

Inhibitors are substances which either markedly retard or at times completely stop enzyme activity. These substances are usually salts of certain heavy metals, strong acids or alkalis and fluorides. Occasionally the accumulation of some products of enzymatic reaction may exert an inhibiting effect upon the enzymes without, however, destroying them.

THE AMYLASES

Amylases are enzymes which catalyze starch hydrolysis, i.e., the conversion of starch into dextrins and maltose. They are found widely distributed in nature, occurring to various degrees in many higher plants,

molds, yeasts, bacteria and in many secretions of the animal body. Depending upon their source, they show variations in certain properties, such as their pH and temperature optima, their thermostability, and resistance to inactivation by acidity, etc. Amylases have been conclusively shown to be protein entities which do not require the presence of co-enzymes for their activity. They are in general quite sensitive to heat and to their chemical environment.

At present two main types of amylases are recognized, alpha-amylase and beta-amylase. Alpha-amylase, acting under favorable conditions,
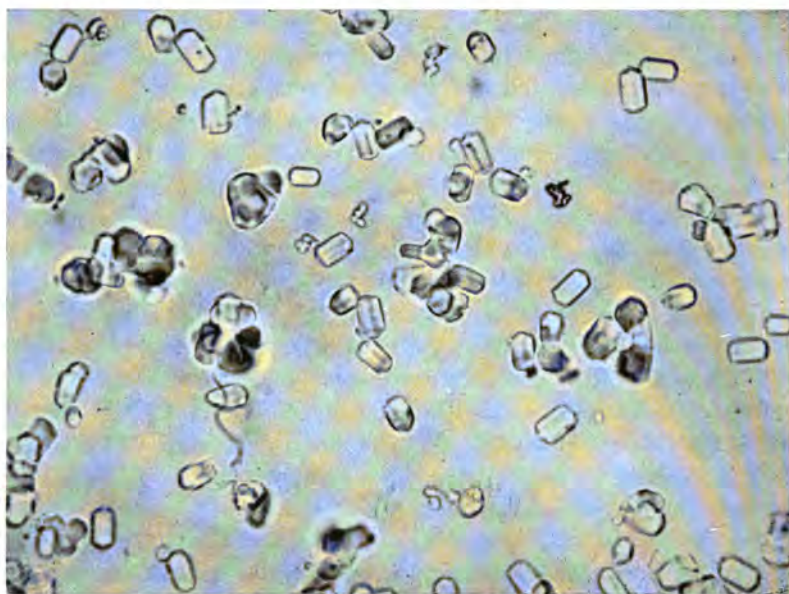
FIG. 13—Crystals of the alpha-amylase of germinated barley. (*Courtesy U. S. Dept. of Agriculture.*)

rapidly splits the starch molecule into smaller dextrins and is therefore also referred to as dextrinogenic amylase. The resulting dextrins do not give a color reaction when treated with dilute solutions of iodine and potassium iodide. Since dextrin formation is accompanied by a marked decrease in the viscosity of the starch paste being acted upon, the enzyme is also called liquefying amylase. The term alpha-amylase is derived from the fact that the dextrins, when examined in a polariscope, exhibit a falling mutarotation, also known as alpha-mutarotation.

Beta-amylase acts upon starch by splitting off maltose sugar and is for this reason also known as saccharogenic or saccharifying amylase. The reaction apparently affects only the side chains of the starch mol-

ecule and comes to a stop while a considerable portion of the molecule is still intact. The resulting dextrins are much larger than those obtained by alpha-amylase action and retain the property of giving a violet to purple color with iodine. The name beta-amylase derives from the rising or beta-mutarotation of the maltose produced by this enzyme.

Aside from their characteristic reactions, these two enzymes differ also in a number of other properties. For example, alpha-amylase acts on native starch and readily liquefies and dextrinizes gelatinized starch with practically no initial production of sugar. Beta-amylase, on the other
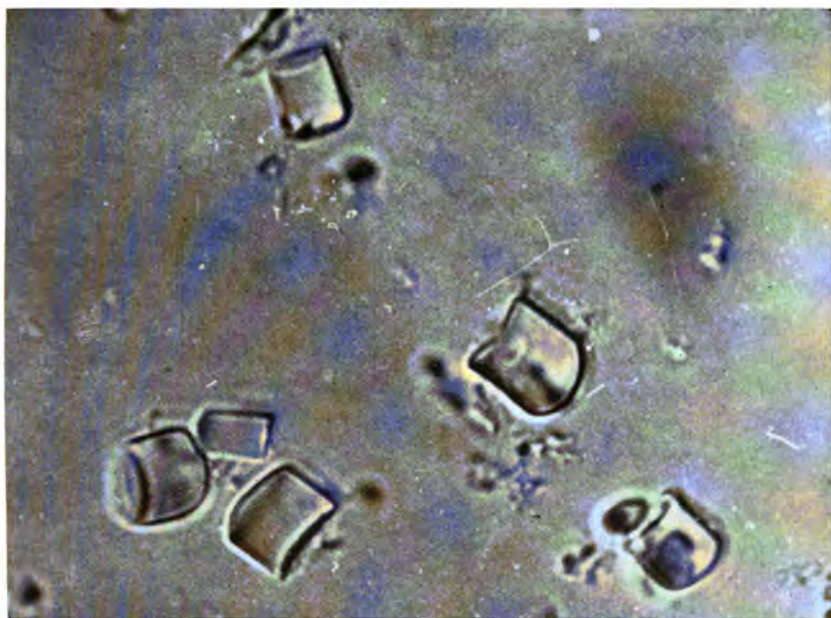
FIG. 14—Crystals of the beta-amylase of germinated barley. (*Courtesy U. S. Dept. of Agriculture.*)

hand, does not act on most native starches and has limited liquefying and dextrinizing action on gelatinized starch. In a purified state, this enzyme produces rapid saccharification but this reaction stops when about 60 percent of the theoretical amount of maltose has been produced. The optimum pH of alpha-amylase activity at room temperature is about 5.0, that for beta-amylase is about 4.5. Alpha-amylase is rapidly inactivated at a low pH, while inactivation of beta-amylase proceeds more rapidly at high pH levels. On the other hand, alpha-amylase is relatively thermostable, being able to withstand exposure to 70° C. (158° F.) under certain conditions without marked loss of activity, while beta-amylase is rapidly destroyed at that temperature. These differences in

properties suggest ways for the selective separation of the enzymes. Thus by holding a mixture of alpha- and beta-amylase for a few minutes at a temperature of 70° C. (158° F.), the beta-amylase is inactivated, leaving the alpha-amylase relatively unaffected in its activity. If the beta-amylase is to be preserved, acidification of the mixture to a low pH will inactivate the alpha-amylase.

Although both amylases are present in sound wheat, the amount of beta-amylase by far overshadows that of alpha-amylase. A considerable proportion of both amylases is in a so-called bound state, that is, it cannot be readily extracted with water or very dilute salt solutions. This bound, or so-called latent, amylase is set free by the action of proteolytic enzymes or by strong salt solutions. It has been shown that of the total amylase originally present in sound wheat, about two-thirds of the beta-fraction and one-half of the alpha-fraction occur in the bound or latent state. When wheat is germinated or allowed to sprout, there is a pronounced production of alpha-amylase, while the increase in beta-amylase is relatively small, indicating that there is only a liberation of the enzyme already preformed in the grain with little or no additional production taking place.

Measurement of Amylase Activity. Efforts to determine the activity of amylolytic enzymes in such products as malt and flour have given rise to a considerable number of specific methods, many of which find wide application in cereal and baking laboratories. Among the best known of these are the Lintner method as modified by Kneen and Sandstedt (*49*), the maltose method of Rumsey (*50*), the gassing power technique (*51*), the Wohlgemuth procedure (*52*), the liquefying method of Jozsa and Johnston (*53*), and the Amylograph method.

The Lintner method as given in the Cereal Laboratory Methods (*54*) provides an indication primarily of the beta-amylase since it is a determination of maltose produced by a flour extract acting upon boiled soluble starch under standard conditions. The Rumsey method also gives a measure of the saccharogenic enzyme. Here a flour suspension consisting of 10 g. of flour in 100 ml. of water is held at a controlled temperature for one hour to permit the flour enzymes to act upon the flour starch and bring about conversion to maltose. The amylases are then chemically destroyed at the end of the reaction period and the maltose produced determined by analysis, with the results expressed in the form of a maltose figure representing milligrams of maltose. The values obtained will range from a maltose figure of about 250 for flour having a low amylolytic action to 400 and more for flours of relatively high amlolytic activity. This method does not take into account the variable amount of fermentable nonreducing sugars naturally present in flours. The gassing power

method is also an indirect measure of the sugar produced by the action of beta-amylase since the gas production measured depends upon the fermentation rate maintained by the rate of sugar production in the dough. The method involves the use of a hermetically sealed chamber attached to a mercury pressure gauge which indicates the gas pressure produced by the fermentation of a flour-water dough. The results are expressed in millimeters of mercury and range between 350 mm. and 500 mm. in the "fourth hour" period for flours of normal amylolytic activity. The correlation between values obtained by the maltose method and the gassing power method is relatively high. However, gas production cannot be predicted accurately from the maltose figure since the maltose method does not measure the initial content of nonreducing sugar, whereas the gassing power method does.

The Wohlgemuth method measures the dextrinogenic or alpha-amylase by determining the change of the iodine staining color produced by its activity. The procedure involves subjecting a buffered starch solution to hydrolysis by the enzyme at constant temperature until the iodine color just disappears. In a modification of the method by Sandstedt, Kneen and Blish, (55) the reaction is allowed to proceed until the iodine treated mixture assumes a definite reddish-brown tint which exactly matches a color standard. The liquefying method of Jozsa and Johnston also gives a measure of alpha-amylase by determining the reduction in viscosity of the starch paste brought about by the dextrinization of the starch.

The amylograph method (cf. p. 521) is designed to measure the effect of amylases on dough at higher temperatures in an effort to approximate the conditions existing during the initial stages of baking when enzyme activity is at its maximum rate. The Amylograph is a recording torsion viscosimeter which measures the gelatinization viscosity of starches. The decrease in viscosity of gelatinized starch by the amylases of malt supplements is correlated with bread quality by baking tests so that the range of amylase activity most suitable for the production of high quality bread can be established by means of the instrument. The instrument is calibrated in arbitrary units representing viscosity on a scale ranging from 0 to 1000, with amylase activity of a flour being inversely proportional to its amylograph value. Flours having a low amylolytic activity are thus indicated by high amylograph values in the range of 900, while flours of normal amylolytic activity will show values of 500 or less. While the amylograph method is much more closely related to the function of amylases in baking practice than the other methods, it requires further study to reveal its full reliability. Anker and Geddes (56) and Johnson, Shellenberger and Swanson (57) have discussed both the tech-

nique and precautions necessary in interpreting the results obtained by this method. Sumner has recently published a brief, nontechnical review and evaluation of the maltose, gassing power, and amylograph methods (*57a*).

Amylase Action in Dough. Enzymatic action is initiated in the dough at the time the dough ingredients are mixed and ceases only after the enzymes are destroyed by the oven heat. This enzymatic action not only provides maltose for yeast fermentation, but induces several changes in dough characteristics, such as a decrease in water absorption capacity, a slackening of the dough, and the development of stickiness. These changes occur as a result of the dextrinization and saccharification of the 3 to 4 percent of damaged starch granules normally present in hard wheat flours. Damage to starch granules occurs during milling and renders the injured granules more susceptible to attack by the amylases. These changes in dough characteristics are particularly noted when diastatic supplements are used since these greatly augment the alpha-amylase activity which is frequently deficient in flours milled from sound wheat. The combined action of alpha- and beta-amylases results in a rapid saccharification, which is of special importance in lean doughs containing little added sugar, as well as in sponge fermentation where sugar is not added until the remix stage. The beneficial effect of diastatic malt supplements is accounted for by the fact that alpha-amylase, which predominates in these supplements and thereby corrects the normal deficiency of this enzyme in flours, rapidly changes the injured starch granules into dextrins and thus makes available an easily converted substrate to the maltose-producing beta-amylase. This is clearly shown by Figure 15 taken from the data of Stamberg and Bailey (*58*) in which doughs without added sugar were baked after various fermentation periods and with and without supplementation by given increments of alpha- and beta-amylases.

The injured starch granules present in flour have a marked water-absorbing capacity. The higher the content of damaged starch in a flour, the greater is its degree of absorption. On the other hand, it has been noted before that the damaged starch is particularly susceptible to amylase action, being readily converted first into dextrins and then into maltose, substances which have a greatly reduced water-absorption capacity. The removal of this starch fraction by amylase action, especially if the flour initially had a relatively large proportion of this fraction and if rather high levels of amylase supplement are employed, will result in a marked reduction in the absorption level of a dough. Consequently, if dough handling difficulties are to be avoided, the use of amylase sup-
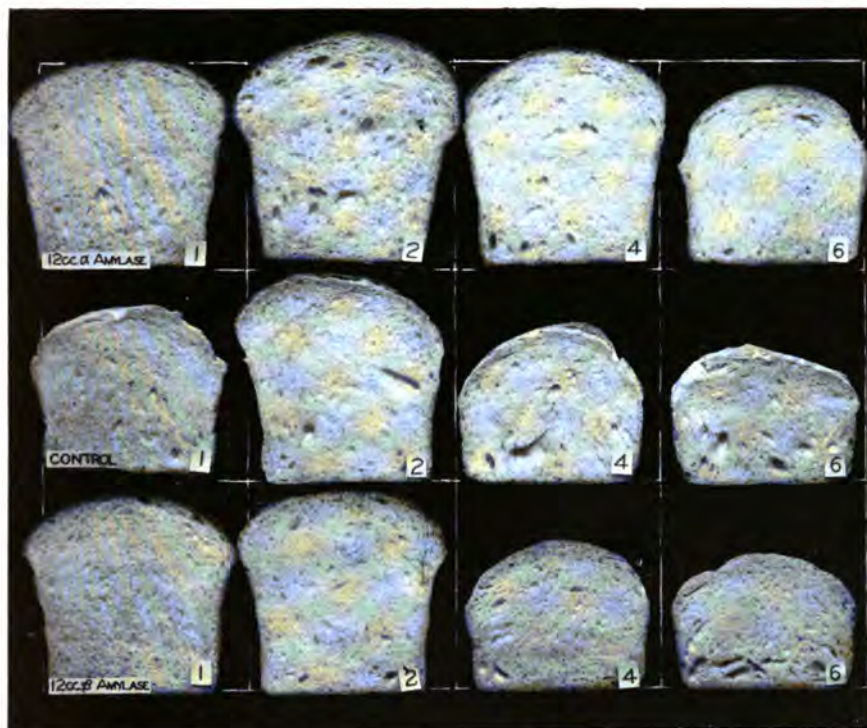
FIG. 15—Influence of alpha- and beta-amylases on loaf volume after various fermentation times in hours. Doughs were fermented and baked without added sugar.

plements should be linked with an appropriate downward adjustment of the absorption.

Stamberg and Bailey (*58*) studied the effect of adding various amounts of alpha-amylase and of beta-amylase to dough on the characteristics of bread. The amylase preparations were so made as to exclude contamination of one enzyme by the other. The alpha-amylase preparations exhibited high dextrinizing activity on soluble starch, while the beta-amylase preparations showed no dextrinizing action but produced rapid saccharification. The addition of a small amount of alpha-amylase preparation to a normal, medium-strength flour dough improved the crust color, grain, and volume of the resulting loaves. The addition of larger amounts increased the loaf volume but produced inferior grain and texture. When beta-amylase was added in larger amounts, the resultant loaves were invariably poorer, showing decreased volume, paler crust color, poorer crumb, and a greater tendency to develop a shell top. Normal flour appears to contain sufficient beta-amylase so that further addi-

tions do not bring about an improvement. When finely pulverized starch was added in amounts of 2 or 5 percent, the diastatic activity of the dough increased as was evidenced by a deeper crust color of the bread, but at the same time the grain and texture were impaired, thus confirming the previous observation of Alsberg and Griffin (*59*) that fine grinding of flours increases the diastatic activity but injures the baking quality.

As already mentioned, amylase activity proceeds throughout fermentation, being favored by the progressive decrease in pH of the dough. The average pH value of doughs going to the oven is between 5.0 and 5.5, which approaches the optimum pH for amylase activity under normal dough conditions. With an increase in dough temperature during the initial stage of baking there is at first a greater increase in the rate of amylase activity than of heat inactivation of the amylases, so that a marked net increase in amylase action results. During the 3 to 4 minutes it requires for the internal temperature of a one-pound loaf to pass through the range from 60° C. (140° F.) to 75° C., (167° F.) a large portion of the starch is gelatinized. The gelatinized starch is rapidly liquefied by alpha-amylase, then in part dextrinized and simultaneously converted into maltose by the action of both enzymes. Beta-amylase is usually inactivated at about 70° C., (158° F.) while the alpha-amylase activity persists to about 75° C. (167° F.). Above that temperature all enzyme activity ceases. This increased amylase activity during the baking stage promotes a desirable oven spring and is highly beneficial to such bread characteristics as crust color, loaf volume, crumb quality and flavor. However, if the dough is over-diastated, excessive conversion of starch to dextrins and maltose may have detrimental effects on the quality of the bread.

The addition of amylase supplements, either to the flour at the mill or to the dough in the bakery, has for its general aim the following effects: (1) Increase in gas production; (2) improvement of crust color; (3) increased moistness of the crumb and keeping quality; (4) better development of flavor; and (5) increased gas retention of the dough and hence larger loaf volume. Supplementation must, however, be carried out judiciously, for excessive amylase activity may cause sticky or runny doughs, yielding loaves with a soggy crumb and reduced loaf volume.

The most commonly used amylase supplements are obtained by the germination of barley and wheat. Originally barley malt was used almost exclusively. In more recent years malted wheat has also prominently come into use. In mill practice the malt is either ground into flour and this flour introduced into the mill stream, or the whole malt is

added to the grain mix prior to milling. While extensive tests have been made with amylase supplements from other cereal sources, such as corn, rye, oats and sorghum, most of these have shown some shortcomings of one kind or another which have acted against their general acceptance.

More recently great interest has developed in purified enzymes preparations from the mold *Aspergillus oryzae* and from certain bacterial sources (*60, 61, 62, 63*). These enzyme preparations contain both alpha- and beta-amylases, as well as traces of proteolytic enzymes. Fungal alpha-amylase has been shown to possess a lower degree of thermostability and bacterial alpha-amylase a higher degree than malted wheat alpha-amylase, which difference accounts largely for their varying activity in flour doughs. Thus whereas fungal alpha-amylase shows little effect on the viscosity of flour suspensions with rising temperatures, the enzyme being inactivated before starch gelatinization has set in, bacterial alpha-amylase, with its high heat stability, has a marked liquefying effect. The different enzyme preparations also show variations in those activities that are measured by maltose value and gassing power tests. Conn, Johnson and Miller (*64*) compared the action of commercial alpha-amylase preparations obtained from two bacterial and six fungal sources with that of malted wheat flour when used as diastatic supplements. They confirmed previous findings that fungal amylase preparations may be used for supplementation if the ratio of proteolytic enzymes to alpha-amylase is not excessive. The two bacterial preparations tested produced a sticky and gummy bread crumb and were therefore unsuitable for supplementation. The results also indicated that the breakdown of starch by amylases from different sources does not proceed along identical lines and that therefore some difference in the final effects is to be expected.

PROTEOLYTIC ENZYMES

The decomposition of the complex proteins into simpler products is accomplished by the hydrolytic action of specific proteolytic enzymes, called proteinases. These enzymes split true proteins into less complex bodies, known as peptides, which in turn are further decomposed by the action of another group of enzymes, the peptidases, into amino acids, the ultimate units of protein structure. The division of proteolytic enzymes (proteases) into proteinases and peptidases may be somewhat arbitrary since most proteinases are known to hydrolyze peptides, but they do so at a much slower rate than when they act upon true proteins. On the other hand, peptidases are generally held to be unable to hydrolyze true proteins. Like the amylases, proteases are of a protein nature and are single entities, i.e., they do not require the presence of coenzymes

for proteolytic action. A considerable number of proteinases have been obtained in crystalline form.

Proteinases are generally grouped into four general types, which are designated as follows by Balls and Kies (*65*):

1. Proteinases most active in neutral or slightly alkaline media (approximate pH optimum 7-8), thus resembling trypsin, the enzyme produced by the pancreas in human and animal bodies. These are frequently called trypsinases or tryptases.
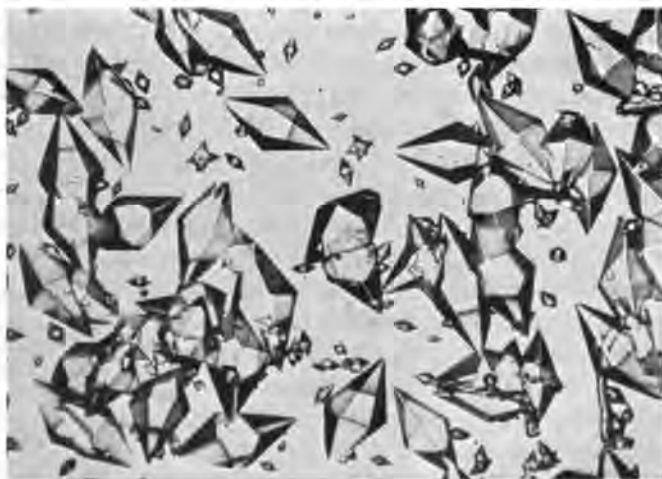
FIG. 16—Pepsin crystals (90 × mag.).

2. Proteinases most active in highly acid media (pH 1.5-2.0), thus resembling pepsin, the enzyme secreted by the gastric glands of the stomach. They have been referred to as pepsinases.

3. Proteinases inactivated by oxidizing agents, and activated by reducing agents. These are the papainases and include the proteinases which occur in wheat and flour.

4. Proteinases of cellular origin, not requiring reduction to an active state, and with pH optima at weakly acid levels (pH 6-7). These enzymes are usually referred to as cathepsins.

We shall concern ourselves primarily with the papain type of proteinase since it is the typical proteolytic enzyme of cereals.

While the presence of proteolytic enzymes in wheat and wheat flour has long been known, it was only in recent years that the proteinase occurring in these products was shown to be of the papain type. The proteinase was characterized by its activation by such reducing agents as cysteine and hydrogen sulfide, and its inhibition by such oxidizing agents as bromate, persulfate and iodoacetic acid. The amounts present

in sound wheat and flour are exceedingly small, but when the grain is sprouted, the quantity of proteolytic enzymes increases considerably. Storage of wheat causes a steady decline of the power to produce proteinase activity on germination, the loss amounting to more than half in two years.

The importance of proteolytic enzymes in flour rests upon their degrading effect upon the gluten of the fermenting dough. It has been shown that when papain is added to a dough, or to the gluten washed from a dough, there develops a marked softening of the dough and a disaggregation of the gluten proteins. Similar effects are observed when flour made from sprouted wheat, which contains high proteolytic activity, is added to a dough. This seemed to indicate that the slackening observed with certain flours during fermentation is attributable to the action of proteolytic enzymes. In recent years this view received strong support from Jorgensen (*66*) and Balls and Hale (*67*). Jorgensen, in advancing his theory of bromate action, held that the dough-improving action of oxidizing agents was due to their inhibiting effect upon the proteinases which otherwise would bring about excessive gluten hydrolysis with the accompanying reduction of gas-retaining capacity in the fermenting doughs. He showed that bromate and iodate, which are flour improvers, inactivate flour proteinases, whereas chlorate, which is not a flour improver, is without effect. The same general conclusions were reached independently by Balls and Hale. These authors (*68*) state that:

"The activity of oxidizing agents in improving the appearance of bread, the effect of oxidants used in bleaching flour, and the improvement that flour undergoes on storage in air can be adequately explained as resulting from the oxidation of the cysteine-like activator. A diminution in the proteolytic activity of the dough is a consequence of such treatment, with the result that the dough of the treated flour does not become as soft as the dough of the untreated and proteolytically more active flour. The difficulties found in preparing a light, spongy loaf of bread from whole wheat flour, or from flour containing wheat germ are probably in part due to the fact that such materials are much richer in proteinase (or else in activator) than is normal white flour."

The detrimental effects of reducing agents, such as glutathione, on loaf volume were explained in the light of the above theory as being brought about by their role as proteinase activators. Thus it was shown that when glutathione, which is in itself devoid of proteolytic activity, is added to a dough, an apparent dough liquefaction is brought about with the result that low-volume bread loaves of unsatisfactory crumb characteristics are produced. The same general effect was obtained when yeast extract was employed instead of glutathione. The loaf volume depress-

ing effect of wheat germ was thus attributed to its high content of glutathione, while the gluten softening occurring during fermentation was ascribed to activators present in yeast.

While the above theory received considerable acceptance in Europe, its reception by American cereal chemists has been less unanimous. A number of discrepancies were disclosed which have not been satisfactorily reconciled with the theory. Thus, for example, it was shown that the harmful effect of germ on dough characteristics and bread quality became progressively less with prolongation of fermentation, whereas according to the theory it should become more marked. The action of glutathione and papain preparations added to dough was shown to be distinctly different. Whereas the papain preparation added to dough induced a progressive softening of the dough with increase in time, the glutathione preparation brought about an immediate softening of the dough which did not increase in time as it should have if glutathione exerted its effects only as an activator of the flour proteinase. Other investigators have shown that there is a direct action of oxidizing and reducing agents on the gluten proteins. Hildebrand *(69)*, after reviewing the large volume of work published on the question of the significance of proteinase in dough fermentation and the conflicting nature of much of the evidence, suggests that the following conclusions appear justified:

"(1) Proteinases are present even in patent flours milled from sound wheat. The concentration of such enzymes in normal flours is low—so low that it is difficult to measure their action accurately and reproducibly. (2) Flour proteinases are of the papain type, and can therefore be activated by reducing agents such as naturally occur in flour, those occurring in other dough ingredients (notably in yeast), or those added experimentally. Moreover, these enzymes may be inactivated by the addition of suitable oxidizing agents such as bromate, chloride, iodate, or vanadate. (3) Despite the analogy between the effect of oxidizing agents on proteinases and their action as bread improvers, it does not necessarily follow that the primary function of improvers is to inhibit the working of flour proteinases."

The same author further suggests that the most probable mechanism for the action of oxidizing agents is an inactivation of the proteinases as well as an oxidative effect directly on flour protein thereby changing its physical properties. The concentration of proteinases in normal flours appears to be too low to have a noticeable effect on gluten properties. For all practical purposes, therefore, the action of oxidizing improvers may be regarded as being a direct one on flour proteins, while their inhibitory action on flour proteinases may be considered of little if any significance.

Peptidases. As pointed out above, peptidases are proteases which act upon decomposition products of proteins. Protein degradation products may range from compounds consisting of only two amino acids, the

so-called dipeptides, to those containing a great number of such units, the so-called polypeptides. Enzymes which hydrolyze dipeptides are termed dipeptidases, while those which attack larger peptides are referred to as polypeptidases. Peptidases are further designated as amino-peptidases, carboxypeptidases, prolylpeptidases and leucylpeptidases, depending on whether a free amino group, carboxyl group, proline or leucine is necessary at one end of the peptide chain for the action of the enzyme. Peptidases in grain include a dipeptidase which splits alanine dipeptides and a leucylpeptidase. Both of these peptidases increase markedly in the grain upon germination. The presence of other types of peptidases in cereals has also been indicated.

OTHER ENZYMES IN BAKING

Esterases. Esterases are enzymes which split fats into simpler products. They are differentiated into lipases or lipolytic enzymes which cleave the glycerides of the fatty acids, and simple esterases which act on esters of fatty acids. In addition to lipase, grains contain such esterases as phytase, which decomposes phytic acid, and phosphatases.

While the presence of fat-splitting enzymes in wheat has been known for years, relatively little research has been done on their nature and activity, principally because they appear to exert little measurable effect upon the baking characteristics of wheaten products. From the limited published data it appears that the wheat lipase is localized in the scutellum and the aleurone layer of the kernel, that its activity increases upon germination as well as upon increase in moisture content. The enzyme is destroyed at a temperature above 60° C. (140° F.). The enzyme appears to act preferentially on the glycerides of fatty acids rather than on the corresponding esters. Deterioration of flour due to rancidity development caused by the action of lipase upon flour fats is of rather rare occurrence. Since rancidity may also be caused by oxidation, it is frequently difficult to decide which form of rancidity is the causative factor of flour spoilage.

Phosphatases are enzymes which hydrolyze various esters containing organically combined phosphorus. They enter importantly into fermentation systems, being indispensable to carbohydrate metabolism of yeast during fermentation. These enzymes, too, have received relatively little study from the viewpoint of their effects during dough fermentation so that their role is far less well known than that of the amylases and certain of the yeast enzymes.

Phytase is an esterase which hydrolyzes phytic acid or phytin into inositol and phosphoric acid or its salts. It exists in a number of cereals, including wheat, in which it appears to be localized in the pericarp. The optimum pH of wheat phytase is close to 5.2.

Phytase has in recent years assumed some nutritional significance with the finding that phytic acid, the enzyme substrate, renders calcium and iron less available for assimilation in the human body. Thus if large amounts of low extraction flour are consumed, considerable phytic acid may be taken in which would greatly limit calcium assimilation. Under these conditions it is generally recommended that the long-extraction flour be fortified with additional calcium, a practice which has been adopted in several countries.

Oxidizing Enzyme Systems. The oxidation-reduction enzyme systems or oxidases play an exceedingly vital role since it is through their action that the energy required for life processes is provided. It is through their intervention that the chemical energy of foods is released in a form that can be utilized by the living cell without an excessive increase in temperature such as results in the more violent and rapid oxidation of fuels. The enzymes accomplish this by catalyzing a step-wise oxidation which passes through a number of phases, each at a slightly different energy level.

The oxidases consist of a so-called activating protein, or enzyme proper, and coenzymes. Representative members of this group are:

Catalase, which catalyzes the decomposition of hydrogen peroxide into water and oxygen. Its probable function is to guard against harmful accumulation of hydrogen peroxide in the grain during germination where an excess of this substance might interfere with normal oxidation-reduction reactions. Catalase activity is markedly reduced in flour by commercial bleaching agents and by aging at room temperature.

Peroxidase, an enzyme which oxidizes a number of amines and phenols in the presence of hydrogen peroxide, is present in all grains. Its function appears to be to prevent the accumulation of certain phenols and amines which might prove harmful to the grain under certain conditions.

Tyrosinase, is an enzyme that catalyzes the oxidation of several phenolic substances, such as phenol, catechol and tyrosine.

Ascorbic-Acid Oxidase acts on 1-ascorbic acid to form dehydroascorbic acid. Ascorbic acid, a reducing agent, has been shown to be able to act as a flour improver. Some investigators hold that the acid is oxidized by the enzyme to dehydroascorbic acid and that the improving effect is due to the latter substance.

Lipoxidase, which oxidizes fats and carotenoid pigments, is important because it accelerates the development of rancidity in fat and causes losses of carotene, vitamin A and ascorbic acid. The bleaching of flour on natural aging is attributable to this enzyme since it acts on the xanthophyll and carotinoid pigments of flour.

CHAPTER V

THE VITAMINS

Introduction. Vitamins are specific organic substances much like the various carbohydrates and proteins. In accordance with this very general definition they partake of the basic characteristics of organic compounds, e.g., they all contain carbon as an essential constituent, they possess relatively complex molecular structures, and their natural occurrence is restricted to plant and animal tissues.

Vitamins are required in minute quantities only to produce pronounced physiological effects. The phenomenal cures of such deficiency diseases as beriberi, pellagra or scurvy obtained by proper dietary changes appeared the more miraculous to early investigators because the curative agents, or vitamins, needed to be supplied only in practically undetectable traces to effect the cures. Thus beriberi, a disease which is prevalent especially in the Far East and in other regions of the world where polished rice constitutes a main food staple, can be prevented by the daily consumption of $\frac{1}{30,000}$ of an ounce of thiamine, so that one ounce of this vitamin will protect eighty people for one year *(70)*. Since the human body is unable to synthesize the majority of vitamins, man must depend upon outside sources, primarily food products of vegetable or animal origin, for an adequate supply of vitamins. More recently, however, it has proved possible to produce many of the known vitamins by chemical synthesis. This has led to the manufacture of vitamin capsules and tablets for supplementary purposes. Furthermore the practice of adding synthetic vitamins, which are identical in every respect to the natural compounds, to such food products as margarine, bread and other cereal products to improve their nutritional value, is gaining increasing acceptance.

Nomenclature. The name vitamin is derived from a very similar term "vitamine" coined by Casimir Funk in 1911. He had obtained a crystalline substance from rice polishings which proved highly specific in the cure of beriberi. Since chemical analysis of this substance revealed it to contain the elements nitrogen and hydrogen, which typify an amine, and since the substance was essential to life, he termed it "vita-amine" or vitamine. Subsequently other substances possessing similar specific effects in other diseases were discovered which, however, did not

contain nitrogen. To render the original term more appropriately applicable to these newer substances, the "e" in vitamine was dropped and the new term "vitamin" applied to all these substances. To differentiate between different vitamins, they were then designated by letters, such as vitamin A, vitamin B, etc. When it was found that several forms of individual vitamins could exist, subscript numerals were added to the letter designations, resulting in such terms as vitamin A_1, A_2, B_1, B_2, etc. More recently, as the exact nature of the various vitamins became known, they were given specific chemical names, such as thiamine, riboflavin, niacin, ascorbic acid, etc. The following list gives both the letter designation and the proper chemical name of the more important vitamins.

TABLE 19. CHEMICALLY IDENTIFIED VITAMINS

Vitamin A —Carotene
B_1—Thiamine
B_2—Riboflavin
B_6—Pyridoxine
B_{12}
C —Ascorbic acid
D —Calciferol
E —Alpha-tocopherol
H —Biotin
K —Naphthoquinone compounds
Niacin
Panthothenic acid
Folic Acid

Functions of Vitamins. The physiological actions of vitamins may be broadly grouped into three general categories: (1) To serve as active components of enzyme or coenzyme systems which control the metabolic and respiratory functions in animal and plant tissues; (2) to prevent the occurrence of pathological or abnormal conditions in the organism; (3) to supply needed materials for the regeneration of certain tissues; (4) to ensure adequate growth in the young.

An example of the first type of function is offered by thiamine. This vitamin has been shown to enter importantly into the intermediary metabolism of carbohydrates. In a modified form it constitutes the coenzyme cocarboxylase which catalyzes the transformation of pyruvic acid into acetaldehyde, an important step in the chain of reactions which ultimately releases needed energy and the by-product carbon dioxide from the body sugar glucose. While pyruvic acid is a normal intermediary product of carbohydrate metabolism, its further breakdown is necessary to bring about the liberation of energy. An abnormal accumu-

lation of pyruvic acid in the absence of a sufficient thiamine intake has been found to be the cause of appetite failure and the decline in gastro-intestinal mobility and general bodily tone which are symptomatic of a deficiency in this vitamin.

The second function of vitamins, namely that of preventing the occurrence of certain pathological conditions in the body, has been the most widely publicized. The precise action of vitamins in their disease preventive role is not as yet fully understood. They appear to act as catalysts in certain vital physiological reactions, which are necessary to the health and proper functioning of bodily tissues. Severe restrictions upon the intake of vitamins may lead to such deficiency diseases as beri-beri (thiamine deficiency) with its accompanying symptoms of nerve paralysis and muscle incoordination, rickets (vitamin D deficiency) with its malformation of bones and teeth, pellagra (niacin deficiency) with its alimentary, nervous and mental disorders, etc.

The third function is that of supplying regenerative substances for tissue use. An example is vitamin A which is needed for the regeneration of visual purple, an eye pigment the bleaching of which in the retina of the eye is one of the chemical reactions involved in vision. Inadequate vitamin A intake leads to so-called night blindness, or the inability to see in dim light.

The fourth important function, namely that of promoting adequate growth in the young, is shared by many of the vitamins. Thus if young animals are fed diets which are devoid of such factors as vitamin A or thiamine, they will exhibit stunted growth and fail to develop into normal-sized adults, in addition to acquiring certain physiological deficiency symptoms.

The vitamins may be grouped into two general categories based upon their solubilities in fat or water. The so-called fat-soluble vitamins include A, D, E, and K. The remaining vitamins constitute the so-called water-soluble group. Aside from the common characteristic of being soluble in the same solvent, there is little other resemblance either in composition or physiological action between the members of the respective categories.

VITAMIN A

Vitamin A is a nearly colorless, oily, fat-soluble substance which occurs in two closely related forms, distinguished as vitamins A_1 and A_2. Vitamin A_1 is found in relative abundance in the fats of milk, egg yolk, salt-water fish liver oils, and animal livers. Vitamin A_2 predominates in the liver oils of fresh-water fish. Normally little distinction is made between the two substances and they are generally referred to by the col-

lective singular term vitamin A. The vitamin is now also being synthesized on a commercial scale.

In addition to these vitamins proper, there are several so-called precursors of vitamin A or provitamins, i.e., substances which are readily hydrolyzed by the body into the vitamin. The known precursors of vitamin A include the yellow pigments alpha-, beta-, and gamma-carotene, and cryptoxanthin. Thus the vitamin A value of a food is determined by both its actual content of this vitamin as well as by its content of provitamins. In general, plant foods, such as vegetables, fruits and cereals owe their vitamin A value chiefly to the presence of precursors. Animal organs, as well as such animal products as butter and eggs usually contain both vitamin A and some precursor.

The accepted structural formula for vitamin A is as follows:

$$H_3C \diagdown \diagup CH_3$$

$$\begin{array}{c} H_3C \\ \diagdown \\ \diagup \\ H_2C \end{array} \begin{array}{c} CH_3 \\ C \\ \diagup \diagdown \\ C-C=C-C=C-C=C-C=C-CH_2OH \\ | \quad | \quad | \quad | \quad | \quad | \quad | \quad | \\ H \quad H \quad CH_3 \quad H \quad H \quad H \quad CH_3 \quad H \end{array}$$

$$H_2C \qquad C-CH_3$$

$$\diagdown \diagup$$

$$C$$

$$|$$

$$H_2$$
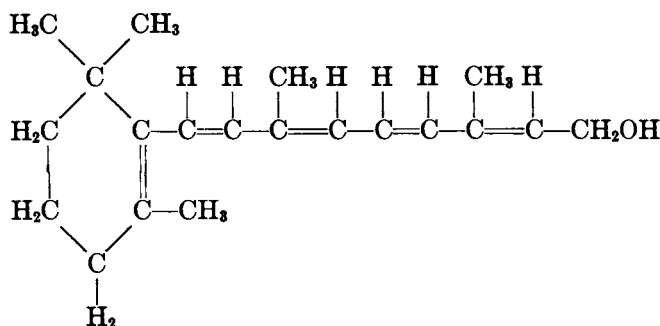
The structural formulas of the carotenes and cryptoxanthin are quite similar to that of vitamin A. They all contain the above ring structure (so-called beta-ionone ring) and differ only in that the hydrocarbon chain is twice as long and ends in an additional ring structure which, in the case of beta-carotene, is identical to the one shown above, while it is different in the other carotenes. Upon hydrolysis, beta-carotene therefore yields two molecules of vitamin A, while the other precursors yield only one each, plus a molecule possessing no vitaminic action.

Vitamin A was discovered in 1913 as a growth promoting factor present in butter fat. Young laboratory animals fed identical diets which were satisfactory in all other respects would continue to grow when the sole fat was butter, but ceased to grow and sickened when the fat was lard which is devoid of the vitamin. Subsequently it was also established that vitamin A was essential to vision, being required for the regeneration of a pigment called visual purple in rod cells of the eye's retina. These cells function in colorless vision and vision in dim light. When light strikes the visual purple it is bleached to yellow and must be regenerated to visual purple before the rods can again become activated

by light. When a shortage of vitamin A exists, this regeneration is retarded which results in difficulties in the individual's adjustment to varying light intensities and vision in dim light. The latter condition is generally known as night blindness. Of equal importance to the above effects of vitamin A deficiency is the relation of this vitamin to mucous membranes which line the respiratory system, the alimentary canal, the urinary tract, eyes and certain secreting glands. These membranes, also called epithelial tissues, undergo certain changes in the absence of vitamin A which greatly weaken their resistance to infection. As a result individuals on diets which are low in vitamin A value are particularly susceptible to respiratory diseases, skin, ear, and sinus infections and inflammations, and infections of the alimentary tract. The skin tends to assume a dry and rough appearance. The condition known as "dry-eye" or xerophthalmia appears in advanced stages of vitamin A deficiency and is characterized by the hardening of epithelial tissues of the eyeball and a failure of the tear glands. The teeth also suffer in vitamin A deficiency through a degeneration of the organs which produce tooth enamel so that a loss of enamel occurs, resulting in the exposure of the dentin and imparting a chalky appearance to the teeth.

Human requirements of vitamin A differ in general with age, bodily weight, and degree of bodily activity. Booher (71) summarizes these requirements as follows: "Allowing for a fair margin of safety and for the maintenance of a moderate storage of vitamin A in the body, a total of around 3,000 (International) units (one I.U. equals 0.6 microgram of pure beta-carotene, and one microgram, in turn, equals one millionth of a gram) of vitamin A daily is suggested for the normal adult (or 1.8 milligrams, one mg. being equal to one thousandth gram). . . . Provision of around 6,000 to 8,000 units (3.6 to 4.8 mg.) of vitamin A daily for the growing child would presumably be adequate to take care of any extra needs associated with growth and development to provide for a moderate bodily storage of vitamin A. A small supplement of some fish liver oil in addition to liberal quantities of whole milk, butter, eggs and green leafy vegetables is recommended for children. . . . The recommended allowance of vitamin A for pregnant and nursing women has been set at around 5,000 units (3 mg.) or more daily. . . ." The National Research Council's Food and Nutrition Board has set the vitamin A requirements at 1,500 units (0.9 mg.) daily for children under 1 year of age, 2,000 units (1.2 mg.) for children 1-3 years old, 2,500 units (1.5 mg.) for those 4-6 years old, 3,500 units (2.1 mg.) for 7-9 year olds, 4,500 units (2.7 mg.) for 10-12 year olds, and 5,000 units (3 mg.) per day for children between 12 and 20 years of age. These quantities will provide a reasonable margin for safety.

The main sources of vitamin A are the green and yellow vegetables, eggs, milk and such milk products as butter, cream, ice cream, cheese, as well as fish liver oils, livers, kidneys, oysters, and red salmon. The following table, adapted from "Agriculture Handbook No. 8," gives the vitamin A values of typical foods:

TABLE 20. VITAMIN A VALUES OF TYPICAL FOODS
(*U.S.D.A. Agriculture Handbook No. 8, "Composition of Foods—Raw, Processed, Prepared." June, 1950*)

Food	International Units per 100 Grams
Green leaves such as kale, spinach, turnip greens	7,000-11,780
Peas, fresh young green	720
Mature seeds generally	nearly negligible
Mill products and breadstuffs	negligible
Sugar and sweets	none or negligible
Fruits: Apples	90
Bananas	430
Cantaloupes	3,420
Oranges	190
Vegetables: Broccoli	3,400
Carrots	12,500
Potatoes	20-50
Sweet potatoes	7,700
Tomatoes	1,100
Turnips	trace
Beef muscle	none
Milk	160
Butter	3,300
Eggs	1,140

THIAMINE

Thiamine, or vitamin B_1, the most thoroughly studied of the vitamins, is a water-soluble, colorless crystalline substance, first isolated in pure form in 1926 and first synthesized in 1936. Space is not available here to trace the highly interesting history of its discovery, the result of years of painstaking observations and experimentations by scientists of many nations. The original impetus was provided by the prevalence of a crippling disease, known as beriberi or polyneuritis, in the Far East where the ordinary diet contains large proportions of polished rice. Water extracts of rice polishings were found to contain a substance active in the cure of beriberi. This substance was isolated by Casimir Funk in 1911 and called vitamin(e). Subsequent studies revealed that Funk's vitamin actually consisted of a whole group of vitamins which was designated as the vitamin B complex. The chemical nature of most of these B com-

plex vitamins is now known and several of them are produced synthetically on a commercial scale.

The structural formula of thiamine hydrochloride is given as follows:

$$CH_3$$

$$N{=}C{-}NH_2HCl \qquad C{=\!=}C{-}CH_2CH_2OH$$

$$CH_3{-}C \quad C{-}\!\!-\!\!-CH_2{-}\!\!-\!\!-\!\!-N$$

$$N{-}CH \qquad\qquad Cl \quad CH{-}S$$
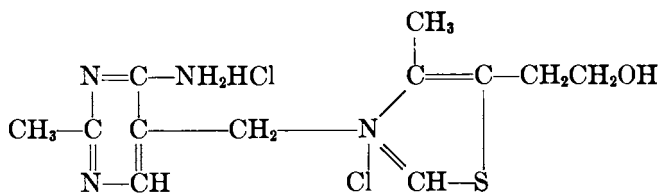
Thiamine (Vitamin B₁) hydrochloride

Thiamine is relatively stable toward oxygen, which inactivates some of the other vitamins, and toward dry heat, but is destroyed by prolonged exposure to wet heat above 212° F., as during cooking, roasting and baking. This destruction occurs to a lesser extent in acid foods than when the foods are close to neutral in reaction. Some investigators hold that the major thiamine losses are due to the vitamin's solubility in cooking waters when the latter are discarded.

Thiamine has been found essential to growth, to proper metabolism of carbohydrates, to the prevention of polyneuritis, to proper nerve function, and to the maintenance of appetite. Numerous animal experiments have shown that an inadequate supply of the vitamin in the young results in stunted growth. This lack of proper growth is partly attributable to loss of appetite which accompanies a subnormal intake of thiamine and results in a reduced general food consumption. Lack of appetite, on the other hand, has been ascribed to another effect of thiamine deficiency, namely the accumulation in the organism of pyruvic acid. This acid is an intermediary product of metabolism for whose further oxidation a certain amount of the enzyme cocarboxylase is required. Cocarboxylase is nothing more than thiamine which has been phosphorylated in the tissues, i.e., to which phosphorus has been added. Most, if not all, abnormal nerve and tissue behavior resulting from thiamine deficiency may be explained on the basis of this incomplete utilization of body fuel, for it is evident that if insufficient energy is provided, the organism cannot function normally. Mild vitamin B₁ deficiency in adults is responsible for much of the constipation, flatulence and dyspepsia which appear with advancing age.

In view of the role which thiamine plays in carbohydrate metabolism, it would be reasonable to assume that the need for this vitamin would depend to some extent upon the amount of carbohydrates consumed by an individual. The greater the carbohydrate intake, the greater should be the amount of thiamine required to bring about its complete conver-
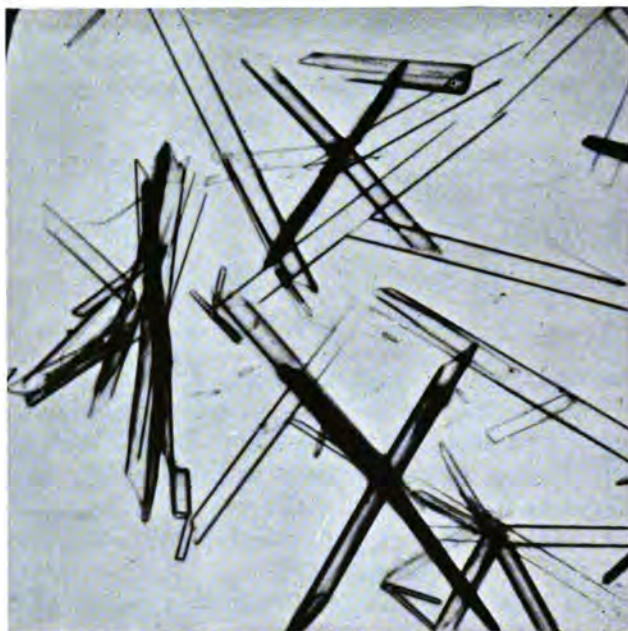
FIG. 17—Crystals of thiamine. (*Courtesy Merck & Co., Inc.*)

sion to energy. The existence of such a direct relationship between calorie intake and thiamine requirement has in fact been established. Cowgill (*73*) has developed a formula for determining the vitamin B_1: calorie ratio which is proportional to body weight. Assuming an average degree of activity and level of daily energy intake, he has calculated that a man weighing 100 pounds requires as a minimum about 135 International units of the vitamin (1 International Unit equals 3 micrograms of thiamine chloride); a person weighing 154 pounds needs approximately 280 International Units, and a still heavier person weighing 200 lbs. requires about 550 International Units. These values must be in the nature of approximations since the exact figure depends very much on the number of calories involved. Borsook (*70*) suggests that an adult should have 5 to 7 International Units of thiamine per pound of body weight per day. In the case of children the daily requirement is about 10 International Units per pound of body weight.

While vitamin B_1 is present in a wide variety of foods, there are few foods that may be considered potent sources of this factor. Vitamin B_1 is not stored in the body to any extent and its requirements must be met each day. The great dependence upon highly refined foods which marks modern dietary habits further contributes to making the adequacy of the thiamine intake a practical problem.

TABLE 21. THIAMINE IN TYPICAL FOODS

(U.S.D.A. Agriculture Handbook No. 8, "Composition of Foods—Raw, Processed, Prepared." June, 1950)

Food	Mg./100 grams
Foods of Animal Origin	
Beef muscle	0.04–0.08
Chicken (and fowl)	0.04–0.10
Lamb (and mutton)	0.12–0.16
Pork muscle	0.48–0.83
Kidney (of cattle, sheep and swine)	0.37–0.58
Liver (of cattle, sheep and swine)	0.21–0.40
Milk	0.04
Eggs	0.08
Egg white	0
Egg yolk	0.27
Grain Products	
Oats (oatmeal)	0.10–0.60
Rice, entire	0.32
Rice, white (polished)	0.07
Wheat, entire	0.43–0.66
White flour (unenriched)	0.08
White bread (unenriched)	0.05
White bread (enriched)	0.24
Whole wheat bread	0.30
Dry Legumes	
Beans, pear or navy, dry	0.67
Beans, Lima, dry	0.21
Peas, dry	0.77
Peanuts	0.30
Other Vegetables and Fruits	
Apples	0.04
Bananas	0.04
Beans, snap or string	0.08
Cabbage	0.06
Carrots	0.06
Lettuce	0.04
Orange (or fresh juice)	0.08
Peas, fresh young green	0.34
Potatoes	0.11
Spinach	0.11
Tomato (or fresh juice)	0.06

Vegetables, including potatoes, constitute an important source of thiamine because of the generally large quantities in which they are consumed. Except for the legumes, which are of relatively high potency, the various vegetables do not show marked differences among themselves in thiamine content. Thiamine tends to be concentrated in the germ portion and outer layers of seeds. Legumes, nuts and whole grains are good food sources. Unenriched refined cereals and white flours, from which the germ and bran portions have been removed, contain little of the vitamin. Foods of animal origin, such as muscle meats, organ meats, milk and eggs, are rated as good sources. One of the richest sources of thiamine is brewers' yeast.

In Table 21, adapted from "Agriculture Handbook No. 8," is given a list of typical foods and their thiamine content in their natural or raw state. It should be remembered that, depending upon cooking conditions, thiamine losses of varying degrees will reduce the actual thiamine content of those foods which are not consumed in their raw state.

RIBOFLAVIN

Riboflavin, also known as vitamin B_2 or G, is an important member of the B-complex vitamins. In its pure form, it is a light, yellow-colored crystalline powder with the unique property of giving a strong yellow-

FIG. 18—Riboflavin crystals. (*Courtesy Merck & Co., Inc.*)

green fluorescence in solution. It is slightly soluble in water and alcohol, and insoluble in such common organic solvents as chloroform, ether and acetone. It is highly sensitive to light and is readily decomposed by both visible and ultraviolet light.

The chemical identification of riboflavin was facilitated by the fact that, when combined with phosphoric acid, it acts as the prosthetic or active group of an important yellow enzyme present in every living cell, at least of higher forms of life, and is concerned with the chemical reactions involved in cell respiration. The structural formula, shown below, reveals riboflavin to consist of ribose, which is a type of sugar and which in the molecule forms the side chain, and of flavin which is a yellow pigment. It was first synthesized in 1936.
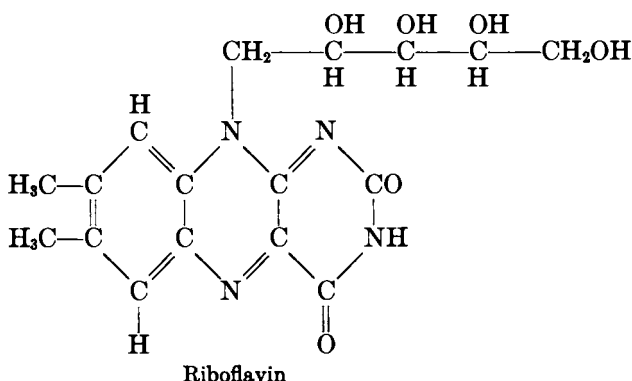
Riboflavin

Because of its important physiological role in cell respiration, one would expect riboflavin to be widely distributed in both plant and animal tissues. It has actually been found, in its enzymic form as a phosphate combined with protein, in such diverse products of life as eggs, milk, meats, eyes, plant leaves, flowers, fruits and seeds. Its isolation from various products before the name riboflavin had been officially adopted, led to such designations, indicative of the source material, as lactoflavin (from milk), ovoflavin (from eggs) and hepatoflavin (from livers).

Sherman (72) has characterized the effects of an inadequate supply of riboflavin as leading to digestive disturbances, nervous depression, general weakness and deterioration of tone, and poor conditions of the eyes and skin. The incidence of infectious disease is likely to be increased, vitality diminished, and the prime of life curtailed by an early development of the physical manifestations of old age.

In terms of more specific symptoms, riboflavin deficiency results in a disease called cheilosis which is characterized by cracking of lips and of the angles of the mouth and certain other facial lesions. This disease

has in the past been confused with pellagra.   Inadequate intake of ribo-
flavin may also result in abnormal changes in eyes which, if not promptly
treated, may lead to permanent injury and impairment of vision.   There
is some evidence that riboflavin may be a factor in the cure of pernicious
anemia.

The human riboflavin requirements have been estimated at between
2 to 3 milligrams daily.   The recommended allowances given by the
Food and Nutrition Board of the National Research Council are as fol-
lows: 2.2 to 3.3 mg. daily for man, and 1.8 to 2.2 mg. for woman; 0.6 for
infants, 0.9 to 1.8 mg. for children under 12 years old, 1.8 to 2.0 mg. for
girls over 12 years of age; and 2.4 to 3.0 mg. for boys in the same age
group.

As indicated previously, riboflavin is widely distributed in nature and
is present in some amounts in most natural foods.   Excellent sources in-

TABLE 22.   RIBOFLAVIN IN TYPICAL FOODS
(*U.S.D.A. Agriculture Handbook No. 8, "Composition of Foods—Raw,
Processed, Prepared." June, 1950*)

Food	Mg./100 grams
Foods of Animal Origin	
Beef muscle.................................	0.15
Pork muscle.................................	0.18
Kidney (beef and pork).......................	0.74-2.55
Liver (beef and pork)........................	2.98-3.33
Milk..	0.17
Eggs..	0.29
Egg white...................................	0.26
Egg yolk....................................	0.35
Grain Products	
Wheat, entire...............................	0.11-0.12
Wheat germ.................................	0.80
Vegetable and Fruits	
Banana......................................	0.05
Broccoli.....................................	0.21
Cabbage.....................................	0.05
Carrots......................................	0.06
Kale..	0.26
Lettuce......................................	0.08
Orange or juice..............................	0.03
Spinach.....................................	0.20
Tomato......................................	0.04
Turnip......................................	0.07

clude organ meats, such as liver, kidney and heart, lean muscle meats, eggs, dairy products, turnip tops, beet tops, kale, germ portions of wheat, peanuts, soybeans and yeast. Among good sources may be included such vegetables as peas, Lima beans, spinach, broccoli, lettuce, cabbage, carrots, beets, and cauliflower; fruits such as pears, peaches, prunes, avocados; and whole wheat and dried legumes. Table 22, cited from "Agriculture Handbook No. 8," gives the average range of riboflavin content expressed in milligrams per 100 grams of food substance of a number of typical foods.

NIACIN

Niacin, or nicotinic acid as it was known until recently, is another member of the B-complex vitamins. It was shown by Joseph Goldberger in 1926 to cure the skin and tongue inflammations which are the most characteristic symptoms of the disease called pellagra. This disease, which usually also results in digestive and nervous disturbances, occurred in the United States principally in the South where the poor subsist on inferior diets. Goldberger called the factor involved in the cure of pellagra the pellagra-preventive factor, or vitamin P-P, pending its chemical identification. In 1937, it was discovered that nicotinic acid and its amide possessed the property of preventing and curing "blacktongue" in dogs which is analogous to pellagra in human beings. Shortly thereafter verification was obtained that Goldberger's vitamin P-P and nicotinic acid, or niacin, were the same substance, possessing the following structural formula:

$$
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{HC} \quad\quad \text{C—COOH} \\
\text{HC} \quad\quad \text{CH} \\
\text{N}
\end{array}
$$
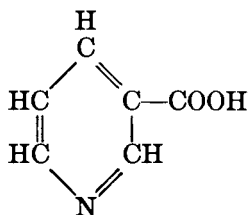
Niacin, when produced synthetically, is a white, crystalline powder. The compound is resistant toward oxidation and is also heat stable. It is only slightly soluble in water, but dissolves readily in alcohol.

Pellagra offers a striking example of what is called a multiple-deficiency disease. The first symptoms to appear are lesions of the alimentary tract. There is loss of appetite with accompanying burning of the tongue. Soon an intense inflammation of the tongue, mouth and gums sets in. The skin becomes rough, reddened and scaly, with sores appear-

ing usually on the backs of the hands, the elbows, knees and ankles. The stomach and intestines become inflamed and the nervous system is affected. These symptoms disappear promptly upon feeding half-gram daily doses of niacin to the pellagrin. However, this cure is only temporary and the symptoms return in from four to six weeks, unless the niacin dosage is supplemented with thiamine and riboflavin. Thus while the major symptoms of pellagra are shown to result from deficiencies of niacin, the condition as a whole requires for its prevention adequate intakes of the entire B-complex of vitamins. Other contributing factors involved in pellagra appear to be inadequacies in the supply of vitamins A, C, and B_6 and of first-class protein. This disease thus typifies the drastic consequences of extreme dietary shortcomings.

The human adult requirement of niacin is at least 10 mg. daily. The recommended allowances of the National Research Council's Food and Nutrition Board provide for 15 to 23 mg. daily for man, and 12 to 18 mg. for woman; 4 mg. for infants, 6 mg. for children 1-3 years of age, 8 mg. for children 4-6 years old, 10 mg. for 7-9 year olds, and 12 mg. for children 10-12 years old. Girls 13-15 years old require 14 mg. daily, and those 16-20 years old 12 mg. For boys in the same age ranges the corresponding requirements are 16 and 20 mg., respectively.

Since pellagra is a multiple-deficiency disease requiring more than one vitamin for its prevention and cure, niacin values of foods are of less significance than are their actual pellagra-preventive values. Foods which have been shown to contain important amounts of pellagra-preventive substances include liver, lean meats, milk and milk products, eggs, fish, tomatoes, green peas, and a variety of green and leafy vegetables.

OTHER B-COMPLEX VITAMINS

Scientists have in recent years discovered several other substances which possess vitaminic activity toward animals and which are accepted as belonging to the B-complex vitamins. Because our knowledge of their nutritional significance to man is in many instances still in a state of uncertainty and subject to experimental verification, these remaining vitamins will be summarized here only briefly.

Pyridoxine. Pyridoxine, also known as vitamin B_6, was first recognized as a substance required by the rat for growth and the prevention of dermatitis. Subsequently it was established that a deficiency of this vitamin produced certain aggravating complications in pellagra. However, our present knowledge of the functions of pyridoxine is still too inadequate to ascribe to it a definite role in human nutrition. There is evidence that in bodily tissues it occurs in combination with a protein and acts as an enzymic catalyst. The pure substance is crystalline in

nature, has a salty taste and is water soluble. It is stable toward acids, alkalies and heat, and has the following structural formula:

$$
\begin{array}{c}
CH_2OH \\
| \\
C \\
\diagup \diagdown \\
HO—C \quad\quad C—CH_2OH \\
| \quad\quad\quad || \\
CH_3—C \quad\quad CH \\
\diagdown \diagup \\
N
\end{array}
$$
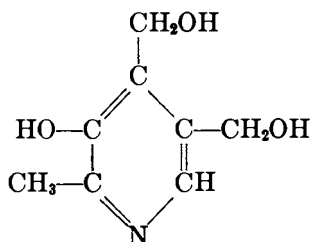
Several compounds related to pyridoxine have recently been shown to possess specific biological activities, indicating the existence of a vitamin B_6 complex. These related compounds or analogs include pyridoxal, which differs from pyridoxine only by having an aldehyde for one of its side groups, pyridoxamine, which contains an amine group (NH_2) attached to one of the methyl groups, and pyracin, identified in an alpha- and beta-form, which contains a carboxyl group.

Among the richest sources of pyridoxine are wheat germ, cornmeal, egg yolk, lard, liver, and the oils of wheat germ, corn, rice, peanut and soybean.

Pantothenic Acid. This vitamin was discovered and named by R. J. Williams in 1939, and identified as a substance widely distributed in nature. Its structural formula is as follows:

$$
\begin{array}{c}
CH_3 \quad OH \\
| \quad\quad | \\
HOCH_2—C———CH—CONH—CH_2—CH_2—COOH \\
| \\
CH_3
\end{array}
$$
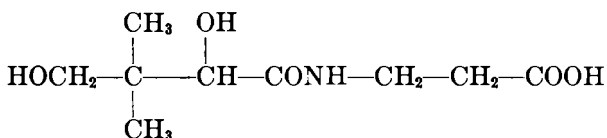
Several investigators in 1940 reported pantothenic acid to be essential to human nutrition and suggested that its function is probably associated with that of riboflavin. It was found that injection of riboflavin into the blood stream causes an increase in the concentration of both riboflavin and pantothenic acid in the blood. Conversely, the administration of pantothenic acid produces an increase of riboflavin as well as of pantothenic acid in the blood. Its actual value in human nutrition has not as yet been definitely established. Relatively good food sources of this vitamin include beef, fish, eggs, yeast, rice, carrots, peas and beans.

Vitamin B_{12}. This new vitamin was first isolated in crystalline form from liver extracts by K. Folkers and his associates in 1948 and given the name vitamin B_{12}. Clinical tests have shown that this vitamin represents the anti-pernicious anemia factor of liver extracts. In its pure

form the material is a red crystalline compound which is required for growth and is one of the most potent microbiologically active factors. Its chemical analysis revealed that it contains cobalt, an essential trace element in hemoglobin formation. Clinical evidence shows that vitamin B_{12} is more effective in the treatment of pernicious anemia than is the vitamin known as folic acid which has been used in treating this disease.

Folic Acid. Folic acid or pteroylglutamic acid, a vitamin essential to growth and the prevention of various types of anemia, was first identified in 1938. It is a nitrogenous acid combining glutamic acid and pteroic acid. The vitamin occurs in natural products as free folic acid and also in the form of various so-called conjugates which exhibit variable vitamin activity. The richest sources of this vitamin are leafy vegetables and liver; most cereal products and muscle meats are rather poor sources. The vitamin is sensitive to cooking and baking conditions so that processed foods may to a considerable degree be devoid of the vitamin.

All of the B-complex vitamins discussed so far have been isolated and their chemical structure determined. A number of additional factors have been postulated whose chemical identity and nutritional significance to man for the most part still remain to be clarified. These vitamins or factors, which have been shown to be essential to certain laboratory animals, chiefly birds, include vitamin B_3, a heat-labile substance required by pigeons; vitamin B_4, a heat-labile factor needed by rats to prevent a certain type of paralysis; vitamin B_5, a heat-stable factor required by pigeons to prevent loss in weight; vitamin B_7 which prevents digestive disturbances in birds; vitamin H or biotin which cures a type of skin inflammation produced in rats by the consumption of raw eggwhite; vitamin J, an anti-pneumonia factor for guinea pigs; factor L, which is required for the maturation of milk-producing tissues; factor M, required by the Rhesus monkey to prevent a certain kind of degeneration of its blood; factor U, apparently required by the chick for growth; factor W, a growth promoting factor for the rat; and the grass juice factor, a substance present in the juices of fresh leaves which possesses nutritional value other than the nutrients already identified.

In considering the nutritional significance of the B-complex vitamins as a whole, it should be kept in mind that these vitamins form a closely associated natural group and that deficiency diseases are seldom due to an inadequacy of a single B vitamin, but are rather the effects of shortages of a number of these vitamins. To guard against deficiencies of these B vitamins it is therefore desirable to rely upon natural foods which supply them in their proper and natural proportions.

VITAMIN C

Vitamin C, also known by its chemical name, ascorbic acid, has the distinction of being the first vitamin postulated as well as the first to be chemically identified. The characteristic deficiency disease of this vitamin is scurvy which ravaged Europe for centuries and which even today makes an occasional appearance in milder forms when a highly restricted diet is imposed upon a population. Early in the eighteenth century it was learned that consumption of fresh vegetables, fruits and germinated cereals prevented scurvy and cured the disease. In 1841 the antiscorbutic property possessed by some foods was explicitly attributed to a definite substance. This represented the first recorded instance in which the existence of a vitamin as a definite, though as yet unidentified substance was postulated. In 1931, or ninety years later, a number of investigators almost simultaneously identified the antiscorbutic substance as a hexuronic acid lactone. The following year it was first successfully synthesized; its structural formula was established in 1933 to be as follows:

$$
\begin{array}{c}
\text{C}=\text{O} \\
|\quad\quad\searrow \\
\text{HOC}\quad\quad\ \ \\
\ ||\quad\quad \text{O} \\
\text{HOC}\quad\quad \\
\ |\quad\ \ \nearrow \\
\text{HC} \\
| \\
\text{HOCH} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$
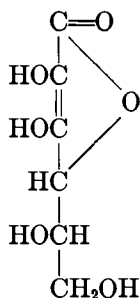
The same year Haworth and Szent-Gyorgyi suggested the name "ascorbic acid" to indicate its antiscorbutic nature, while the American Medical Association recommended the name "cevitamic acid."

Ascorbic acid, now produced synthetically from several monosaccharide sugars to which it is closely related, is a white, crystalline substance, which melts at 192° C., (377.6° F.) is readily soluble in water, soluble in alcohol, and insoluble in oils, chloroform or ether. While relatively stable when in the dry state, it is readily oxidized when in alkaline solution. Oxidation, which is greatly accelerated by exposure to air, light and heat, and certain metallic catalysts, such as copper, entails the complete loss of the vitamin's activity.

Although the pathological effects which result from a deficiency of ascorbic acid are well recognized, the actual physiological function of the vitamin in the human body is still only partly understood. It is known

that many of the symptoms of scurvy are attributable to abnormalities which result in intercellular materials from a vitamin C deficiency. Under normal conditions, body cells, such as those of connective tissues, lie in an amorphous substance in which extremely fine fibers or fibrils are formed. These fibrils, in turn, become cemented together into wavy bands of collagen by a translucent matrix, the transformation being suggestive of the setting of a gel. In the absence of vitamin C, the cells themselves and the amorphous substance are apparently unaffected, but there is a failure in the production of the exeremely fine fibrils or collagen. A supply of ascorbic acid will almost immediately result in the reappearance of translucent bundles and masses of collagenous materials. The formation of intercellular material of bone and teeth is similarly controlled by vitamin C.

The decline or failure of the tissues to produce intercellular material as a result of a shortage of vitamin C is held to be largely responsible: (1) for weakness of the blood vessels and consequent hemorrhages which may occur anywhere in the body; (2) for faulty dentine formation in teeth which entails profound changes in the structure of the teeth and gums; (3) for changes in the growing ends of bones, leading to deformities similar to those occurring in rickets; (4) for a weakening of the bone structure due to loss of supporting cartilage and of calcium; (5) for degeneration of muscle fibers, leading to extreme weakness; and (6) for anemia caused by the destruction of blood-forming cells in the bone marrow. Ascorbic acid deficiency can thus lead to multiple and drastic results so that even after manifest or severe scurvy has been eradicated, vitamin C will remain a vital factor in nutrition.

Blood analysis tests for ascorbic acid content have revealed that if the level of vitamin C in blood plasma falls below 0.5 mg. per 100 cc. there is danger of scurvy developing. A normal and adequate level is 1 mg. or more per 100 cc. If the value is between 0.5 and 1 mg. it is considered to be a borderline case requiring increased vitamin C intake. The National Research Council's Food and Nutrition Board has recommended a daily allowance of vitamin C as follows: 75 mg. for man; 70 mg. for woman, except during pregnancy and lactation when it is 100 mg. and 150 mg. respectively; for children under 1 year old it is 30 mg.; 1-3 years old, 35 mg.; 4-6 years old, 50 mg.; 7-9 years old, 60 mg.; 10-12 years old, 75 mg. Girls between the ages of 13 to 20 years require 80 mg. daily, and boys in the same age group 90 to 100 mg.

Among the chief food sources of ascorbic acid are the citrus fruits and tomatoes. Other good sources are raw cabbage, strawberries, fresh raw turnip, fresh green peas, asparagus, radishes, beans, lettuce, potatoes, liver, brain and kidney.

It should be remembered, however, that the method of storage, cooking and canning of foods has an important bearing on their ascorbic acid content because of the ease with which this vitamin is inactivated through oxidation.

VITAMIN D

Vitamin D, discovered in 1918, is the factor which controls proper bone development. A deficiency of this vitamin results in rickets, a disease which is prevalent in childhood and which, if permitted to progress into later years, may result in permanent deformity and other serious after-effects.

At present some ten closely related substances are known to possess antirachitic or rickets-preventing properties. Of these five have thus far been chemically identified; but only two are of outstanding importance, namely vitamin D_2, which is activated ergosterol and is also known as calciferol, and vitamin D_3, or activated 7-dehydrocholesterol. Ergosterol, the vitamin D_2 precursor, is of plant origin, while the closely related substance 7-dehydrocholesterol is of animal origin. These precursors do not possess antirachitic properties, but are readily converted or activated into their vitaminic form by irradiation with ultraviolet light. The presence of such vitamin D precursors in the human skin accounts for the fact that prolonged exposure of the body to sunlight or ultraviolet lamps, as in sun-bathing, prevents and cures rickets.

The generally accepted structural formula of calciferol is as follows:
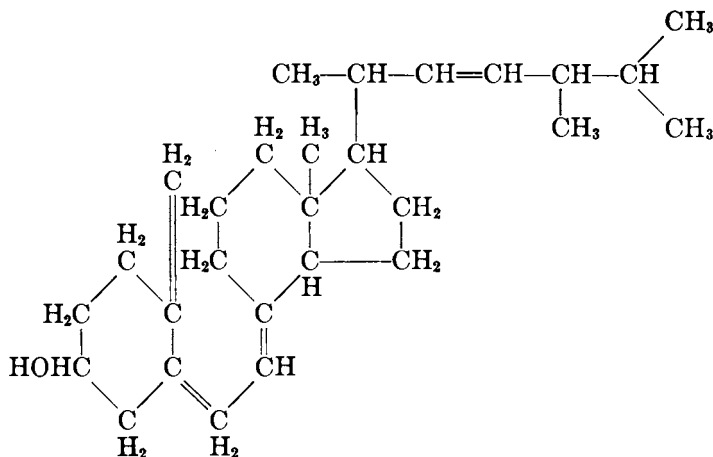
The formula for vitamin D_3 is identical except that its side chain does not contain the double bond (the two carbon atoms each carry a pair of hydrogen atoms instead), and the methyl group on the next to the last carbon of the chain is replaced by a hydrogen atom.

The D vitamins share with the sterols certain common characteristics, namely solubility in fats and fat solvents and insolubility in water. They are quite resistant to the processes of canning and cooking.

Vitamin D functions primarily in controlling the amount of the minerals calcium and phosphorus, the main bone-forming materials, in the blood. For the prevention of rickets, therefore, adequate intakes of both the vitamin and of the two minerals are essential. Because of this interdependence of these factors, it is quite possible for rickets to develop even in the presence of adequate amounts of vitamin D, if there exists a deficiency of either calcium or phosphorus or both. In the absence of normal amounts of calcium and phosphorus in the blood, caused either by a deficiency of vitamin D or an inadequate intake of the minerals, there is less than normal deposition of these materials at the growing zones of bones. The zones become widened and the bone structure softens and becomes unable to bear normal strains without deforming. Children suffering from severe rickets will show the following general symptoms: a squarish head, bad teeth, a pigeon-breast with wide flaring ribs, and bowlegs. If the disease is cured early in childhood, no permanent deformities of the bones result. If it prevails into late childhood the defects can no longer be corrected.

The recommended daily allowance of vitamin D by the National Research Council's Food and Nutrition Board is 400 to 800 International Units for all age groups (10 to 20 micrograms). The minimum human requirement has been estimated to be at 300 to 400 International Units per day.

The main sources of vitamin D are fish liver oils and irradiated ergosterol. Sun-bathing and exposure of body to ultraviolet lamps also possess important antirachitic effects. Common foods which contain important amounts of vitamin D include egg yolk, whole milk—especially if irradiated, butterfat, fortified margarines and cereals. The use of vitamin D concentrates requires some caution since excessive dosages of this vitamin entail harmful results.

OTHER FAT-SOLUBLE VITAMINS

Vitamin E. About the time when vitamin D was being identified, various workers established the existence of another fat-soluble vitamin which proved essential for normal reproduction. This factor was first called vitamin E, and later identified to be a tocopherol. At present, three such substances are recognized as possessing vitaminic function, the most potent being alpha-tocopherol. Its structural formula is as follows:

$$CH_3-C \diagdown \diagup C \diagdown \diagup C-(CH_2)_3-C-(CH_2)_3-C-(CH_2)_3-C-CH_3$$
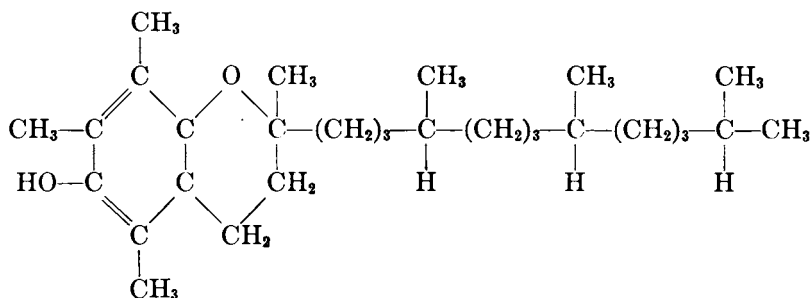
A severe deficiency of vitamin E will lead to irreversible degeneration of the germinal epithelium in man and result in permanent sterility. In woman such a deficiency prevents normal pregnancies. This condition can, however, be corrected by an adequate vitamin E intake so that no permanent sterility results. The tocopherols are rather widely distributed in nature and are powerful antioxidants, i.e., they retard the oxidation of the oils with which they are naturally associated. Vitamin E, though stable in most other respects, is rather easily destroyed by oxidation, especially in the presence of iron salts which act as catalysts. It occurs abundantly in wheat germ oil and is found in many other foods, so that severe deficiencies are quite rare, being encountered only with unusually restricted diets.

Vitamin F. The term vitamin F was formerly applied to the nutritionally essential fatty acids, linoleic and linolenic acids. However, the use of this term has been discontinued and these acids are no longer recognized by the medical profession as vitaminic substances.

Vitamin K. In 1929 the Danish investigator Dam observed subcutaneous, or internal, bleeding in chicks raised on an artificial diet. He further found that the blood of such chicks took an abnormally long time to clot. Six years later he established the lack of a fat-soluble vitamin K as the cause of these symptoms. Since then it has been shown that this substance is widely distributed in green leaves and two forms of it have been chemically identified. They are derivatives of a substance known as 1.4-naphthoquinone. Synthetic products, possessing nearly equal effectiveness, are now being produced commercially.

Vitamin K functions in normalizing the clotting power of the blood by controlling the production of prothrombin in the blood. The reactions involved in blood clotting, which consists essentially of a conversion of fibrinogen to an entangled interlacing network called fibrin, is as follows: The fibrinogen is converted by an active agent called thrombin. Thrombin does not as such exist in blood but is present in an inactive form

called prothrombin. To convert the inactive prothrombin into the active thrombin requires the interaction of a substance called thrombokinase and of calcium ions. By controlling the production of prothrombin in blood, vitamin K thus also controls the clotting reaction.

Vitamin K is found abundantly in green leaves, spinach, alfalfa, and green cabbage, and is synthesized by intestinal bacteria in man and several animals. It is also manufactured commercially. Deficiencies of this vitamin are most likely to occur in infants and in adults who suffer from a deficiency of bile which appears to be essential for the absorption of vitamin K into the blood.

THE ENRICHMENT PROGRAM

The recognition of the nutritional significance of vitamins, coupled with the results of American dietary studies which revealed that large segments of the population were subsisting on diets dangerously low in certain of the B complex vitamins, eventually led to official endeavors toward improvement. These, in 1941, crystallized in the recommendation by the Food and Nutrition Board of the National Research Council that white flour and white bread be fortified with certain specified increments of thiamine, riboflavin, niacin and iron, with additions of calcium and vitamin D being optional. While the program for enriching white flour and white bread met with a favorable and widespread acceptance on the part of millers and bakers, the Food Distribution Administration (later merged into the War Food Administration), a federal agency established shortly after America's entry into World War II for the purpose of assuring the best possible utilization of the nation's food resources, made the enrichment of all white bread compulsory in its first order issued in December 1942. Since at that time no formal definition for enriched bread had been adopted, enriched bread was to be made from enriched flour, already standardized in May 1941, or to have the equivalent ingredients added to it during the preparation of the dough. On the other hand, the enrichment of all white flour did not become mandatory, partly because of the opposition of many bakers who preferred to enrich bread in their own plants and partly because of other considerations. Exceptions occurred in states which passed state enrichment legislation covering both bread and flour.

The original levels of vitamin and mineral contents in enriched flour and bread were based upon the presumed levels at which these nutrients occurred naturally in whole wheat. Because commercial production of riboflavin was at first inadequate to meet the needs which total enrichment would impose upon the industry, the mandatory inclusion of this vitamin was deferred until such time when adequate supplies became

available. There were also subsequent modifications of the levels of the various vitamins as more refined vitamin assay methods permitted their more accurate estimation.

The final standards, which became effective on ·October 1, 1943, and which still apply at the time of this writing for enriched flour and enriched bread, are summarized in the following tabulation.

TABLE 23.   ENRICHMENT STANDARDS
(Mg./lb., unless otherwise stated)

	Flour		Bread	
	Min.	Max.	Min.	Max.
Thiamine..................	2.0	2.5	1.1	1.8
Riboflavin................	1.2	1.5	0.7	1.6
Niacin...................	16.0	20.0	10.0	15.0
Iron.....................	13.0	16.5	8.0	12.5
Calcium*.................	500	625	300	800
Vitamin D, U. S. P. units*...	250	1000	150	750

* Optional ingredients.

A word in explanation of the different levels of enrichment of flour and bread may be in order here. The important food item is bread rather than flour, since the latter must first be converted into bread to become edible, or at least palatable. The vitamin intake is thus governed by the vitamin content of bread as the ultimate product consumed. Bread contains on an average about 37 percent of moisture, compared with a normal moisture content of 13 percent for flour. In addition, bread also contains certain other ingredients of a non-farinaceous nature. As a result, white fresh pan bread contains approximately 66 percent of flour by weight. In general, therefore, the enriching ingredients present in enriched bread are about 66 percent of those in enriched flour. Stated differently, if enriched flour is to be used for the production of enriched bread, the flour must contain approximately one third more enriching ingredients on a per pound basis if the required level is to be attained in the bread. An exception is formed by thiamine which suffers a loss during baking averaging 10 to 12 percent.

The enrichment program lost its mandatory character with the termination of the War Food Administration's existence, except in those states which had adopted state regulations requiring bread and flour enrichment. However, the majority of bakers have continued to adhere to the program which continues to draw support from government bodies and nutritionists and indications are that it will become a permanent feature of American baking practice.

CHAPTER VI

YEASTS, MOLDS AND BACTERIA

Introduction. The baking process, as will become abundantly apparent in the course of this treatise, involves a highly complex interplay of physical, chemical and biological reactions. Of these perhaps the most important, and certainly the most fundamental, is the fermentation process brought about by the life activities of a unicellular plant, the microscopically small yeast cell. The activities of yeast, however, are not the only biological phenomena of consequence with which the baker is concerned. From a negative standpoint, the molds and bacteria, constituting the less desirable microflora normally encountered in bakery plants, also occupy a position of some importance. While the yeast plant and its aerating and maturing action on flour doughs have received intensive study by baking scientists ever since yeast was recognized as the fermenting agent, interest in molds and bacteria in their relation to the baking process and to baked goods has been less pronounced and sustained, except for brief and occasional intervals when outbreaks of serious fungal or microbial infections of baked goods led to financial losses and health problems.

In the present chapter, an attempt will be made to summarize first the more basic and significant data about yeast as the primary biological agent, and then to review those aspects of molds and bacteria which are essential to an adequate understanding of these microorganisms as they affect bakery operations.

THE YEASTS

Classification. Botanists inform us that at present some 250,000 distinct species or individual types of living plants have been discovered and described. In the presence of such a vast array of plant types, it is evident that the Botanical Sciences would today be hopelessly mired in utter chaos had not some orderly system of classification been devised which groups all members of the plant kingdom into categories of various magnitude, the individual members of which possess common characteristics. Plants which have many characteristics in common are placed in a small category. Several small categories are in turn grouped into a larger category in which greater differences between the members are apparent

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These larger categories themselves are assigned to a still larger category. This process continues until all plants are grouped in a manner which coincides with our views of their degrees of resemblance or difference.

Modern taxonomy, or science of classification, was firmly established by Carl Linaeus (1707–78), the Swedish botanist who first introduced a brief, graphic method of formal description for each type of plant and animal. He was also first to attach a formal Latin designation to each type of organism which was to remain its official scientific name. This Latin name is a double one (i.e., it is a binomial). It consists of the name of the genus, which is always given first and is capitalized, followed by the name of the species. By thus combining the generic and specific names it is possible to assign to each known species a title that is distinctive. *Saccharomyces cerevisiae*, can refer to but one thing, namely, the species *cerevisiae* (which includes baker's yeast varieties) of the genus *Saccharomyces*, which constitutes a group of true yeasts.

While the use of the Latin binomial serves to provide a distinctive name for each type of organism, it would still fall short of its purpose if the systematic arrangement of the categories within categories were left only to the arbitrary decisions of individual botanists. Obviously some fundamental concept upon which to base the classification is required. The guiding concept adopted by modern taxonomy is that of evolution. The accepted system of classification attempts to reflect the degree of descent or relationship between categories of organisms. Thus all species thought to have been derived from a relatively recent common ancestor are placed into the same genus; all genera thought to have descended from a more remote common ancestor are placed into the same family; and so forth. We thus have a scheme of classification which, beginning with the species, ascends through the genus, tribe, family, order, class, and culminates in the four great divisions of the plant kingdom, namely the Thallophytes, Bryophytes, Pteridophytes, and Spermatophytes. Not all taxonomists, however, adhere consistently to this classification, preferring sometimes to employ intermediate categories, such as "sub-genus" and "sub-family," and further designating groups smaller than the species as "varieties," "races," and "sub-species."

With this brief introduction, we may now attempt a more meaningful placement of yeast in the realm of the plant kingdom. Of the four major divisions listed above, the Thallophytes, or more technically *Thallophyta*, comprise the simplest types of plants. The first part of the name is derived from "thallus" which signifies a plant body in which differentiation into roots, stems and leaves, such as is found in higher plants, is lacking. Since the yeast cell corresponds to such an undifferentiated plant body, yeasts obviously belong to the division of the Thallophytes.

The Thallophytes comprise the Algae, the Fungi, and the Bacteria. These types of organisms, while they possess many common characteristics, differ in several fundamental respects. Thus, for example, the algae are so-called independent organisms, while the fungi are dependent organisms. This differentiation is based upon their mode of food acquisition. The algae, containing chlorophyll, are capable of synthesizing their food from inorganic compounds, with the aid of energy supplied by sunlight, in a process called "photosynthesis" (cf. Carbohydrates). In this respect they resemble the higher plants. The fungi, on the other hand, lack chlorophyll and depend for their food upon organic matter synthesized by other organisms. This characteristic of dependence upon other organisms they share with practically all of the animals, including man. Fungi are further differentiated into saprophytes, which utilize lifeless organic material, and parasites which prey directly upon the bodies of living organisms. Yeast, being devoid of chlorophyll, is a dependent organism and is classified with the fungi. The particular species of yeast which includes baker's yeast utilizes sugars for its energy needs and therefore comes under the category of saprophytes. There are, however, several yeast-like species which are parasitic and are the causative agents of several infectious diseases.

The subdivision Fungi is further divided into four classes. These are Basidiomycetes, Ascomycetes, Phycomycetes, and Fungi Imperfecti. This division is made on the basis of sexual reproduction as well as other differences. While a detailed discussion of these classes is beyond the scope of this volume, a summarized treatment will be found in the section on Molds.

The yeasts are commonly grouped with the Ascomycetes. This group as a whole is characterized by possessing an "ascus" or sac. This ascus, which at first is a simple cell, undergoes a series of divisions, involving nuclear and cytoplasmic matter, to yield a group of usually eight spores. Yeast has been included in this class because it may on occasion form an ascus-like sac of spores, although its usual form of reproduction is by a vegetative process.

The Ascomycetes, in turn, are divided into a number of families, one of which is *Saccharomycoideae* or yeasts. This family consists of several tribes of related yeasts and yeast-like organisms, including the tribe *Saccharomycetaceae*, which are the true yeasts. The genus comprising the various industrial yeasts used for such fermentation processes as baking, brewing, wine making, distilling, etc., is *Saccharomyces*, and the specific yeast type is *Saccharomyces cerevisiae*. This species is further subdivided into varietal strains and races, indicating still narrower adaptations of the yeasts to specific functions. Thus while bakers' yeast and

brewers' yeast both belong to the species *Saccharomyces cerevisiae*, they cannot be interchanged if best results are to be obtained in either baking or brewing.

It should be kept in mind that while the accepted system of classification is based on the concept of evolutionary descent of the organisms, many individual species are encountered which deviate markedly in many of their characteristics from the common properties possessed by the group as a whole to which they have been assigned. Their inclusion in a given group is therefore questionable and subject to differences in opinion. A case in point is that of the yeasts. Yeasts are included among the Fungi, yet they lack the ability to form mycelial growth which is one of the basic structural characteristics of the fungi. Yeasts are further classified among the Ascomycetes, yet it is only rarely that they reproduce by means of ascospores which is typical of this group as a whole. In fact, their normal mode of reproduction by the process of "budding" is unique, with only one or two exceptions, among the fungi. Thus while the present system of classification is extremely useful and indispensable to a meaningful study of biology, it is by no means perfect.

Morphology of Yeasts. Yeasts are difficult to define because of the many variants which exist. Thus it is often impossible to decide with any degree of exactitude whether a specific organism, in which a single character normally found only in true yeasts is combined with other properties not found in any other yeasts, should properly be included among the yeasts or not. Henrici's statement that "yeasts are true fungi whose usual and dominant growth form is unicellular" (74), while satisfactory, fails on the one hand to exclude certain primitive fungi which are unicellular but are not yeasts, while on the other hand it does not include certain yeast-like forms which produce mycelial growths. Any all-inclusive description of the characteristics of all accepted yeasts would be largely meaningless. Since we are interested mainly in but one species, *Saccharomyces cerevisiae*, the following comments are to be understood to refer only to that particular species, unless otherwise indicated.

When a drop of yeast suspension is examined with a microscope a great number of yeast cells is seen. These cells occur mostly in an isolated state, i.e., as single entities, except for occasional short chains consisting of three to four cells. Each cell represents a distinct individual organism capable of an independent existence and of producing new cells and colonies. Yeast is thus a unicellular fungus.

The shape of the cell varies with different species, but is usually round or ellipsoidal in the case of *S. cerevisiae*. Some yeasts (*S. pastorianus*, among others) have elongated, sausage-shaped cells, while the cells of

S. ellipsoideus are prevalently elliptical. However, cell shapes of inter-mediary form are frequent so that varieties cannot be reliably identified solely on the basis of the shape of their cells. A marked variability in cell size also exists, depending on such factors as variety, growth con-ditions, age of cells, etc. The range of dimensions is generally within 1 to 10 microns in length and 1 to 8 microns in width.

Structurally, the yeast cell, in common with other plant cells, consists of a differentiated protoplasm contained in a cell wall. There is a single nucleus, sharply delimited from the rest of the protoplasm by a definite membrane. The cytoplasm, or the jelly-like matrix in which the nucleus is embedded, is marked by the presence of numerous granules and vacuoles representing various types of reserve foodstuffs. The entire proto-plast is bounded by a lifeless perme-able cell wall which, atypically for a plant cell, does not consist of cellulose but of hemicellulose and yeast gum. It serves the multiple functions of giving shape to the cell, affording some protection to the very delicate proto-plast, and permitting the movement in and out of the cell of liquids, dissolved food substances and waste products. In young cells, the cell wall is ex-tremely thin and transparent to the point of being invisible, but it thickens considerably as the cell ages. At the same time, the granular character of the protoplasm becomes more sharply defined and old cells may become fairly filled with irregularly shaped granules and vacuoles.

FIG. 19—Diagram of a typical yeast cell. (*Courtesy Wallerstein Labora-tories.*)

The protoplast is encased in the plasma membrane whose apparent function is to exercise a selective permeability. In other words, whereas the cell wall is permeable to nearly all solutes, the plasma membrane per-mits the passage of certain dissolved substances only. It thus controls the passage of nutrients into the cell and of metabolic products out of it.

The nucleus is a dense particle of protoplasmic matter, surrounded by a nuclear membrane. It is readily stained with proper dyes. Its shape is usually oval, but may also assume a kidney-shaped form. It is a rather tiny body, usually less than 1 micron, but may occasionally ac-quire a size of 2 to 2.5 microns in diameter. Because of its extreme

smallness, relatively little accurate information is available about its internal structure or its constituents. The nucleus plays a vital role in the general metabolic activities of the cell as a whole and is a carrier of hereditary characteristics. It contains the highly complex hereditary factors, the chromosomes. Attempted analyses of the chromosomes tend to indicate that they contain nucleic acid and a high-molecular protein. Each chromosome carries a certain number of so-called genes, which are the factors that determine specific properties of the organism such as cell shape, fermenting power, etc. Cell reproduction is intiated by the nucleus which divides into two individual parts, one of which migrates into the so-called daughter cell, carrying with it an identical complement of chromosomes and genes as is found in the nucleus remaining with the mother-cell. The actual mechanism of nuclear division need not be discussed here.

The carbohydrate reserves of the yeast cell are stored in vacuoles in the form of glycogen rather than starch. This also is atypical, since glycogen is characteristically an animal starch. Its presence in the yeast cell is readily demonstrated by the reddish brown color it yields when the yeast is treated with an iodine solution.

Oily or fatty substances appear in yeast as highly refractile vacuoles. They vary greatly in size, being numerous and small in young cells, and tending to coalesce into fewer but larger granules as the cell matures and ages. Certain species of yeast show a marked propensity for fat formation and give rise to fat vacuoles which frequently fill nearly the entire cell. In some European countries such yeasts have been grown on carbohydrate waste products specifically for their high fat content during periods of food scarcities.

The yeast cell contains as reserve material another substance known as volutin or metachromatic material which is stained by methylene blue. It occurs both in the protoplasm as well as in vacuoles in the form of granules. Volutin is now thought to be identical with yeast nucleic acid and appears to have some connection with the cell's fermentative activity, since it is most abundant in vigorously fermenting yeast.

Protein occurs in the cytoplasm in the form of very fine granules. Proteins isolated from yeast include albumin, globulin, phosphoproteins, nucleoproteins, lecithoproteins and glycoproteins. Others may possibly be present. Yeast also contains a number of protein derivatives such as peptones and amino acids.

Chemical Composition. From a chemical viewpoint, yeasts contain from 68 to 83 percent of moisture, the average for baker's yeast being close to 73 percent. The protein, carbohydrate, fat and mineral contents

vary within a rather wide range, depending upon the type of yeast and on the conditions under which it is grown. C. N. Frey (*75*) has prepared the following table showing a typical analysis of the dry matter of yeast:

TABLE 24.   CHEMICAL COMPOSITION OF THE DRY MATTER OF YEAST

	Per-cent		Per-cent
		Ammonia	8
Protein.............	52.41	Purine and pyrimidine bases	12
		Diamino acids	20
		Monoamino acids	60
Fat.................	1.72		
Glycogen............	30.25	Phosphorus pentoxide	54.5
Hemicellulose, gum,		Potassium oxide	36.5
etc...............	6.88	Magnesium oxide	5.2
		Calcium oxide	1.4
		Silicon oxide	1.2
Ash................	8.74	Sodium oxide	0.7
	———	Sulfur trioxide	0.5
	100.00	Chlorine and iron	trace

According to this table, protein and glycogen constitute about 82 percent of the total dry matter of yeast. Among the minerals, approximately 91 percent consist of phosphorus and potassium compounds, some seven other inorganic compounds making up the remaining 9 percent. The following elements, in their inorganic combinations, have been found to be either essential or beneficial to yeast growth: Potassium, magnesium, phosphorus, sulfur, chlorine, calcium and iron. Not all of these elements are of equal importance, although the quantities in which they are present in yeast are not always indicative of their essentiality.

Block and Bolling (*76*) recently published a comprehensive analysis of the amino acid content of yeast protein. While interest in this subject has persisted since the beginning of the present century—largely because yeast has a high protein content and is economically produced and therefore serves as a ready source of a high-protein supplement to feed rations and human dietaries under emergency conditions—it is only in relatively recent years that amino acid analyses have yielded reliable results. In Table 25 by Block and Bolling the percentage composition of yeast protein and muscle protein, in terms of essential amino acids, is compared.

The above figures reveal a striking similarity in the amino acid composition of yeast and that of muscle protein. Yeast protein is thus shown to contain all of the essential amino acids and to be a biologically complete protein.

TABLE 25. ESSENTIAL AMINO ACID COMPOSITION OF YEAST
PROTEIN AND MUSCLE PROTEIN

Amino Acid	Crude Yeast Protein	Muscle Protein
	%	%
Arginine..........................	4.3	7.1
Histidine........................	2.8	2.2
Lysine...........................	6.4	8.1
Tyrosine.........................	4.2	3.1
Tryptophane.....................	1.4	1.2
Phenylalanine...................	4.1	4.5
Cystine..........................	1.3	1.1
Methionine......................	+	3.3
Threonine.......................	5.0	5.2
Leucine..........................	13.2 ± 2.6	12.1 ± 1.1
Isoleucine.......................	3.4 ± 0.2	3.4 ± 0.2
Valine...........................	4.4 ± 0.8	3.4 ± 0.4

Asexual Reproduction of Yeasts. The most commonly observed mode of reproduction in *S. cerevisiae* is by the process of budding. In this process the mature yeast cell forms a small protuberance, or bud, which gradually increases in size. Cytoplasm and nuclear material migrate from the original cell, called the mother-cell, into the bud. After the bud has reached a certain size, it becomes constricted at its base and a wall forms, separating the new cell, the so-called daughter-cell, from the mother-cell. The new cell may become detached immediately from the mother-cell and begin to go through the same process on its own. Occasionally, the new cell remains attached to the mother-cell, forms a new cell by budding, which also remains attached and, in turn, produces a fourth cell, thereby giving rise to the short typical chains that are observed with the microscope. Since in this type or reproduction there apparently occurs an equal division of the chromosomes, the new cell will in all aspects be similar to the original mother-cell. This fact has been utilized in the establishment of so-called pure culture yeasts which are derived from a single original yeast cell possessing the desired fermenting and keeping qualities.

Yeasts of the species *S. cerevisiae* also reproduce by a process of sporulation. Under certain conditions, the cell of the yeast becomes a kind of sac or ascus in which spores are formed. These spores are generally referred to as ascospores and also as endospores, being formed within a cell. In ordinary sporulation the nucleus of the cell divides repeatedly, giving rise, in the case of baker's yeast, to four new nuclei. Each new nucleus is then surrounded by dense cytoplasmic matter and finally by a membrane. Sporulation occurs most readily under condi-
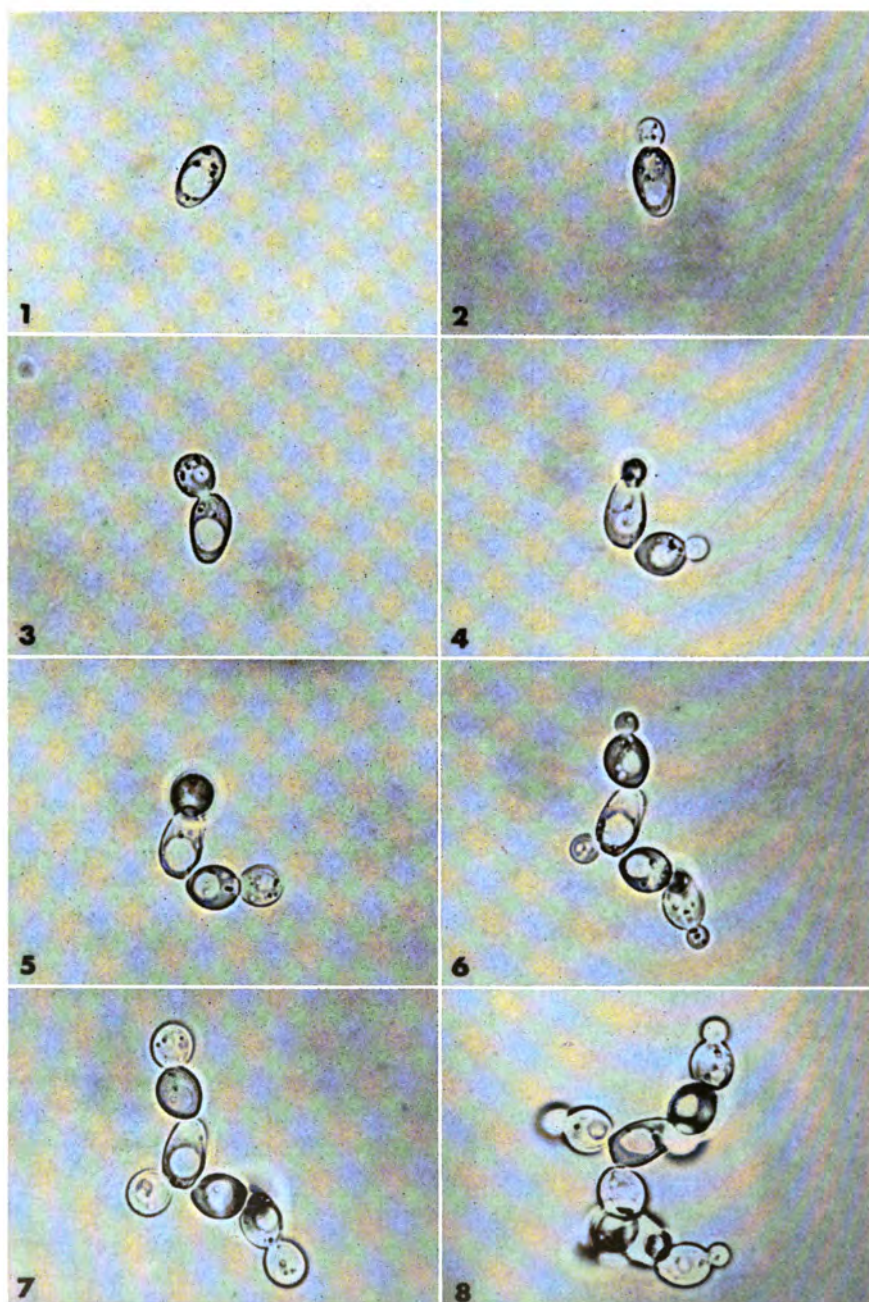
Fig. 20—Yeast Growth. Series of microphotographs showing vegetative yeast propagation. Photographs show growth stages, beginning with single yeast cell, at 15 minute intervals (1,000 x mag.). (*Courtesy Fleischmann Laboratories.*)

tions of adequate moisture and free access to air. After the ascospores have attained a certain size, the old cell wall bursts and releases them. The spores then germinate into new cells which can then again reproduce by budding. It is seen that there is no involvement of sexes in this process of ordinary sporulation.

The ascospores are in some respects analogous to bacterial spores, being resistant to heat, drought and other unfavorable environmental conditions which would prove fatal to the vegetative cell. However, they lack the extreme hardiness of bacterial spores and are readily killed by short exposures to temperatures above 60° C. (140° F.) The main difference between ascospores and bacterial spores, however, is that ascospores result from a process of multiplication, whereas bacterial spore formation is primarily a preservative device, i.e., multiplication does not as a rule occur.

For the sake of completeness it should also be mentioned that some species of yeast of the genus *Schizosaccharomyces* are capable of reproduction by so-called binary fission, or equal division. When the cell has reached a certain size, the nucleus divides into two equal portions and a transverse wall is formed between the two new nuclei, resulting in two daughter-cells. These two new cells may either separate immediately or remain in physical contact for a while and, on subsequent divisions, give rise to short chain formations. This mode of reproduction is essentially the same as occurs in bacteria.

Sexual Reproduction. While sexual reproduction in some yeasts was first recognized about 1902, the *S. cerevisiae* were generally considered to be without sex, or parthenogenetic. Beginning in 1935, however, the Danish scientists Winge and Laustsen, in a series of definitive papers, established beyond doubt that the industrial yeasts of the genus *Saccharomyces* are capable of conjugation in their vegetative state, and that conjugation or fusion occurs also among their spores upon germination. Spores which germinate without fusion give rise to so-called haploid cells, in which the nucleus contains only half of the full number of chromosomes; such cells are usually smaller and tend toward a globular form. Cells resulting from spores which have fused are so-called diploid cells which possess a full complement of chromosomes; these cells tend to be larger and have an elongated shape. Winge and Laustsen (77) also showed that spore formation in a yeast is associated with a genetic segregation that makes the spores in any ascus genetically different. This fact has been established in many species of the genus *Saccharomyces* by isolating all four spores contained in an ascus by means of a micromanipulator and then allowing them to germinate. The individual pure cultures derived from the four spores turn out to differ distinctly,

as is apparent from the series of illustrations of giant colonies in Figure 21.

The fact that many yeasts undergo a process of fertilization in the course of sporulation, through the fusion of the spores by pairs, makes it possible to produce hybrids of yeast (*78*). Hybridization of different yeasts is arranged by placing in a droplet of culture medium two haploid spores of different species so as to enable them to fuse, forming a diploid
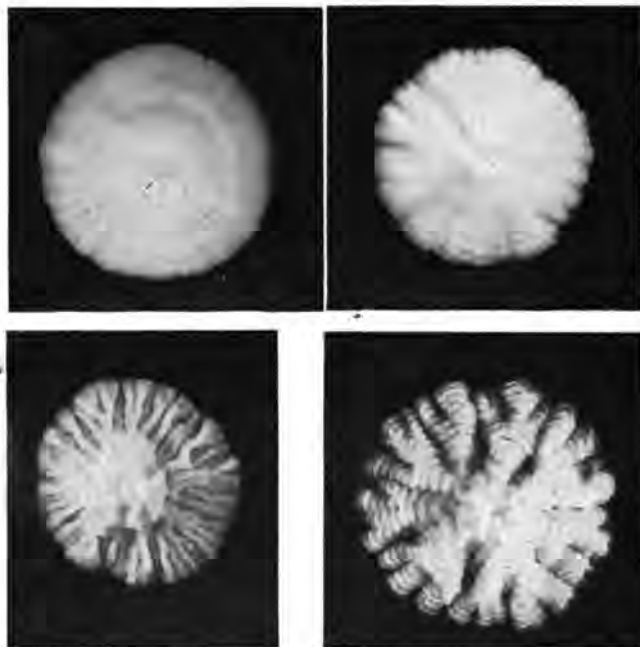
FIG. 21—Example of genetic segregation. Upper left picture shows giant colony of original bakers' yeast. Remaining pictures show colonies grown from three spores separated from single cell of original yeast. (*Courtesy O. Winge.*)

zygote from which the hybrid yeast germinates. This procedure is illustrated in Figure 22. In the first microphotograph a spore from a *S. cerevisiae* (bakers' strain) variety has been placed next to a spore of *S. validus*. A few hours later the two spores have fused into a zygote (second microphotograph) on which a bud is forming which represents the new hybrid. Figure 23 illustrates the corresponding giant colonies: Bakers' yeast is shown in the upper left hand corner, the colony of *S. validus* in the upper right hand corner, and two colonies of the hybrid are shown in the second row.

The work of the Danish scientists has been verified and extended in this country by Carl Lindegren and Gertrude Lindegren (*79, 80*). These

investigators, in repeating Winge and Laustsen's hybridization method, found that "copulation usually fails (1) if the spores are of the same mating type, (2) if either of the spores germinates directly into a diploid
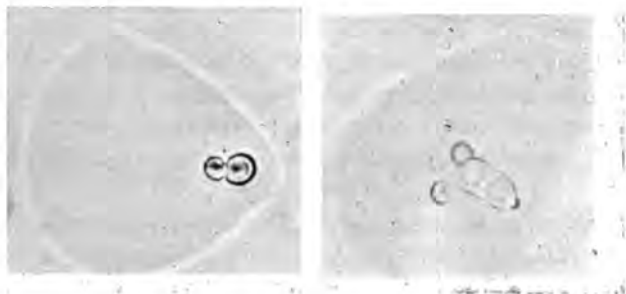
FIG. 22—Experimental hybridization. Two spores from different yeasts are placed in droplet of culture medium (at left). A few hours later they have fused into zygote from which new hybrid forms. (*Courtesy O. Winge.*)

cell (this happens rather frequently, especially in vigorous strains), (3) if either spore is inviable (viability is generally about 50 to 75 percent)." As a result of these facts relatively few hybrids are obtained by ascospore to ascospore matings. Lindegren and Lindegren (*81*) developed a

FIG. 23—Results of hybridization: Giant colonies of bakers' yeast shown at upper left; *S. validus* at upper right. Two colonies of the hybrid are shown in lower row. (*Courtesy O. Winge.*)

new procedure based on the fact that some single ascospores from *S. cerevisiae* produce persistently haploid cultures. They found it possible to hybridize these with other haploid cultures of complementary type by mixing the cells in an appropriate medium. A large number of matings is thereby obtained.

The importance of these new studies in yeast genetics and hybridization for the baker lies in their practical application. Thus it is now possible to produce new yeast hybrids selected especially for their desirable characteristics, such as greater keeping quality and greater baking strength.

The Mechanism of Fermentation. Alcoholic fermentation may be defined as the enzymatic conversion of carbohydrates into alcohol and carbon dioxide. Although it was one of the earliest of human discoveries, it is only within about the last century and a half that scientific interest has centered upon elucidating the actual chemical reactions involved in this process. In 1789 Lavoisier first succeeded in drawing up a fairly accurate equation between the quantities of carbon, hydrogen and oxygen present in the original sugar and in the resulting alcohol and carbon dioxide. Some twenty years later Gay-Lussac proposed his classic equation of fermentation which is still retained at present to account for the principal products of fermentation:

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH + 27 \text{ calories}$$

100 parts glucose	48.9 parts carbon dioxide	51.1 parts alcohol
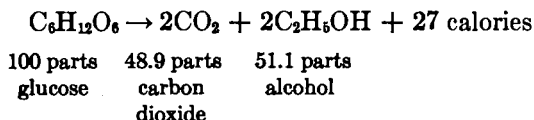
The studies of Louis Pasteur on yeast greatly augmented our knowledge of fermentation. He was able to show conclusively that alcoholic fermentation is caused by the yeast cell in the absence of oxygen and enunciated the general principle, "Fermentation is life without air." He also found that the Gay-Lussac equation does not hold exactly quantitatively since it fails to account for certain by-products of fermentation. Among the normal by-products he found small quantities of succinic acid, glycerol, fatty materials and other undetermined matter.

Eduard Buchner subsequently established that the intact yeast cell was not essential to fermentation by showing that fermentation could take place in the presence of yeast juice pressed from the cells. However, the living cells are the only known source of the enzyme system zymase which effects the transformation of sugar to alcohol and carbon dioxide.

While the Gay-Lussac equation gives both the initial material and the principal end-products of alcoholic fermentation, it tells nothing of the reaction involved in bringing about this rather far-reaching conversion. No attempt can here be made to give in detail the various theories which

at one time or another have been proposed in explanation of the intermediary reactions of fermentation, nor is it possible to indicate the real contributions made to this subject in the last three decades by scores of physicists, chemists and enzymologists whose combined efforts have resulted in a clarification of all the intermediary phases which appear to satisfactorily explain the entire conversion of sugar to alcohol and carbon dioxide. This discussion, therefore, will be limited to a brief summary of the basic scheme of fermentation now generally accepted and referred to as the Embden-Meyerhof scheme, using as a guide the outline given in Table 26 (*82*).

There are three fermentable simple sugars or monosaccharides, namely —glucose, fructose, and mannose. A fourth, galactose, is not ordinarily fermentable except under conditions where yeast has been able to adapt itself to this monosaccharide. Starch or glycogen within the cell is also susceptible to fermentation after a preliminary splitting into a glucose-phosphate ester. This process is called a phosphorolysis and involves the action of an enzyme known as phosphorylase which forms a complex with adenylic acid and magnesium. The end-product of the reaction is glucose-1-phosphate, the so-called Cori ester. This ester is then transformed into glucose-6-phosphate, the Robison ester, by the enzyme phosphoglucomutase.

When extracellular starch is subjected to fermentation, it must first be hydrolyzed by amylolytic enzymes into glucose and fructose. The enzyme hexokinase then catalyzes the phosphorylation of the glucose to glucose-6-phosphate and of fructose and mannose to their respective 6-phosphates. The phosphate group required for this reaction is provided by a coenzyme—adenosine triphosphate, which is changed in the process to adenosine diphosphate. As will be pointed out later, the triphosphate is restored in subsequent reactions. The glucose-6-phosphate is transformed into fructose-6-phosphate, the so-called Neuberg ester, by the enzyme hexose isomerase.

It is seen that the first step in fermentation is thus a phosphorylation of the sugars into esters of phosphoric acid. What is more, all subsequent intermediary products up to the point when pyruvic acid appears are phosphorylated products. Otto Meyerhof (*83*) suggests as a reason for this that by means of phosphorylation the oxidative energy of fermentation is stored in energy-rich phosphoric groups and is made available from these for all syntheses concerned with life, growth and function of the cell. The enzymes which catalyze phosphorylation are by no means restricted to yeast, but are found in muscle, animal organs, bacteria, and typical plants, indicating that phosphorylation is a basic reaction in the metabolism of all forms of life.

TABLE 26. SCHEME OF ALCOHOLIC FERMENTATION

STARCH or
GLYCOGEN + PO₄   GLUCOSE + PO₄   FRUCTOSE + PO₄

   Phosphorylase   (Adp)   (Adp)
   Adenylic acid   Hexokinase   Hexokinase
   Mg⁺⁺   Phosphogluco-   Hexose
            mutase   isomerase

GLUCOSE-1-PHOSPHATE ⇌ GLUCOSE-6- ⇌ FRUCTOSE-6-
(Cori ester)   PHOSPHATE   PHOSPHATE
               (Robison ester)   (Neuberg ester)

                               + PO₄

FRUCTOSE-1,6-DIPHOSPHATE
(Harden-Young ester)

                             Aldolase

PO₄ + 3-PHOSPHOGLYCERALDEHYDE ⇌ DIHYDROXYACETONE
(Fisher ester)   Isomerase   PHOSPHATE

      (Nonenzymatic?)
      ± H₃PO₄

1,3-DIPHOSPHOGLYCERALDEHYDE (?)

      Coenzyme 1
      ± 2H

1,3-DIPHOSPHOGLYCERIC ACID

      Adenosine diphosphate

3-PHOSPHOGLYCERIC ACID + adenosine triphosphate

      Phosphoglyceromutase

2-PHOSPHOGLYCERIC ACID

      Enolase
      ± H₂O

PHOSPHOENOLPYRUVIC ACID + H₂O

      + Adenylic acid

PYRUVIC ACID + Adenosine triphosphate

      + Carboxylase

ACETALDEHYDE + CO₂

      + Reduced coenzyme I
      ± H₂

ETHYL ALCOHOL

The next step in the fermentation process is the conversion of fructose-6-phosphate, which is a hexose monophosphate, into fructose-1,6-diphosphate, a hexose diphosphate, by the introduction of a second phosphate group. The enzyme catalyzing this phosphorylation is phosphohexokinase and here again adenosine triphosphate provides the required phosphate group, being dephosphorylated to a diphosphate in the process.

It might not be amiss to inject here the explanatory remark that the numerals in the ester designations refer to the carbon atoms to which the phosphate groups are attached. Recalling the structural formula of fructose as developed in the chapter on The CARBOHYDRATES, fructose-6-phosphate and fructose-1, 6-diphosphate would thus have the following formulas:

$$
\begin{array}{c}
CH_2OH \\
| \\
C{=}O \\
| \\
HO{-}C{-}H \\
| \\
H{-}C{-}OH \\
| \\
H{-}C{-}OH \quad O \\
| \quad \nearrow \\
CH_2OP{-}OH \\
\searrow \\
OH
\end{array}
\qquad
\begin{array}{c}
\quad\quad O \\
\quad\quad \nearrow \\
CH_2OP{-}OH \\
| \quad \searrow \\
C{=}O \quad OH \\
| \\
HO{-}C{-}H \\
| \\
H{-}C{-}OH \\
| \\
H{-}C{-}OH \quad O \\
| \quad \nearrow \\
CH_2OP{-}OH \\
\searrow \\
OH
\end{array}
$$

<div align="center">Fructose-6-phosphate   Fructose-1,6-diphosphate</div>
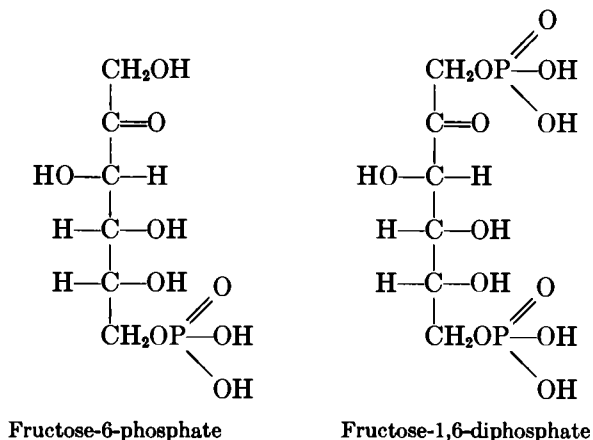
In other words, in the first case the phosphate group is attached to carbon No. 6, while in the second formula a phosphate group occurs at both the first and the sixth carbon atom of the molecule. Fructose-1,6-phosphate is also known as the Harden-Young ester, having first been isolated by A. Harden and W. J. Young in 1908.

This ester is next split by the enzyme aldolase or zymohexase into two trioses (compounds with but three carbon atoms), dihydroxy acetone phosphate and 3-phosphoglyceraldehyde, according to the following reaction:

$$
\begin{array}{c}
CH_2OPO_3H_2 \\
| \\
C{=}O \\
| \\
HO{-}C{-}H \\
| \\
H{-}C{-}OH \\
| \\
H{-}C{-}OH \\
| \\
CH_2OPO_3H_2
\end{array}
\xrightleftharpoons{+H_2O}
\begin{array}{c}
CH_2OPO_3H_2 \\
| \\
C{=}O \\
| \\
CH_2OH
\end{array}
\rightleftharpoons
\begin{array}{c}
CH_2OPO_3H_2 \\
| \\
CHOH \\
| \\
CHO
\end{array}
$$

<div align="center">Fructose-1,6-phosphate   dihydroxy acetone phosphate   3-phospho-glycer-aldehyde</div>
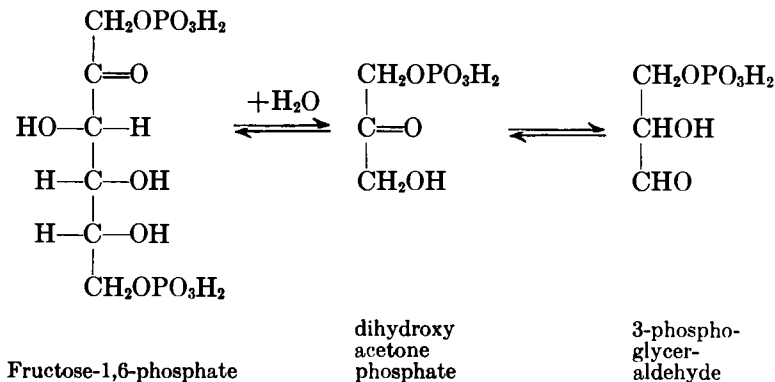
The 3-phosphoglyceraldehyde is subsequently converted into 1,3-diphosphoglyceraldehyde through the introduction of another phosphate group, undergoing at the same time an oxidation to yield 1,3-diphosphoglyceric acid. This reaction is catalyzed by apozymase, whose coenzyme I, also known as cozymase, undergoes a corresponding reduction. This cozymase is of considerable interest since the vitamin niacin amide forms an essential component of its structure. The 1,3-diphosphoglyceric acid is then dephosphorylated by adenosine diphosphate to 3-phosphoglyceric acid, the adenosine diphosphate being converted in the process into the triphosphate and thus again becoming available for the phosphorylation of the glucose, fructose and mannose to their respective 6-phosphates which, as has been seen, constitutes the initial reaction of fermentation.

The 3-phosphoglyceric acid is the mother substance of ethyl alcohol. The enzyme phosphoglyceromutase brings about a change within the molecule of the substance by shifting the phosphate group from the third to the second carbon atom, forming 2-phosphoglyceric acid. The enzyme enolase carries the reaction one step further by removing one molecule of water to yield phosphoenolpyruvic acid. This double reaction may be illustrated as follows:

$$
\underset{\substack{\text{3-Phosphoglyceric}\\\text{acid}}}{
\begin{array}{l}
\mathrm{CH_2{-}O{-}P{\overset{\displaystyle O}{\diagdown}}{-}OH}\\
\mid \qquad\qquad\diagdown\,\mathrm{OH}\\
\mathrm{CHOH}\\
\mid\\
\mathrm{COOH}
\end{array}}
\;\rightleftharpoons\;
\underset{\substack{\text{2-Phosphoglyceric}\\\text{acid}}}{
\begin{array}{l}
\mathrm{CH_2OH}\quad\;\mathrm{O}\\
\mid\qquad\quad\diagup\!\diagup\\
\mathrm{CHO{-}P{-}OH}\\
\mid\qquad\diagdown\,\mathrm{OH}\\
\mathrm{COOH}
\end{array}}
\;\rightleftharpoons\;
\underset{\substack{\text{Phosphoenol-}\\\text{pyruvic acid}}}{
\begin{array}{l}
\mathrm{CH_2}\qquad\quad\mathrm{O}\\
\parallel\qquad\qquad\diagup\!\diagup\\
\mathrm{C{-}O{-}P{-}OH}\\
\mid\qquad\quad\diagdown\,\mathrm{OH}\\
\mathrm{COOH}
\end{array}}
$$
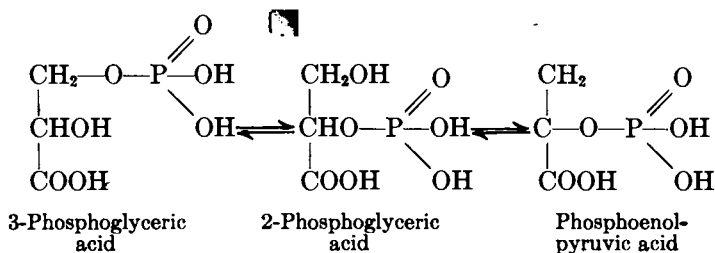
Phosphoenolpyruvic acid is next dephosphorylated by the enzyme dephosphorylase to yield pyruvic acid. The phosphate group made available may be accepted either by adenylic acid to bring about the restoration of the adenosine triphosphate, or by glucose or glucose-6-phosphate, both of which act as phosphate acceptors as was shown during the initial stages of fermentation.

Pyruvic acid is decarboxylated by the enzyme carboxylase, yielding carbon dioxide, which is one of the principal fermentation products, and acetaldehyde. Carboxylase contains a coenzyme, known as cocarboxylase, which has been shown to be a diphosphate of thiamine. Acetaldehyde is reduced to ethyl alcohol, the other principal end product of fermentation, the reaction being catalyzed by cozymase which serves as the hydrogen carrier. The hydrogen required for this reduction is made available by the oxidation reaction in which 1,3-diphosphoglyceraldehyde is converted into 1,3-diphosphoglyceric acid.

The above outline of the scheme of alcoholic fermentation has been reduced to the simplest form consistent with an enumeration of the major intermediary phases. No mention has been made of the numerous side-reactions which occur and which lead to the formation of a wide variety of by-products, such as glycerin, certain organic acids (including lactic, succinic, glyceric and formic acids), higher alcohols, esters, acetaldehyde, ammonia, and so on. All these by-products seldom amount to more than 6 percent of the total fermented sugar in normal fermentation.

The agents or factors within the yeast which are responsible for bringing about the conversion of sugar to carbon dioxide and alcohol are generally referred to as zymase. It has been seen that zymase is not a single enzyme, but a complex system consisting of enzymes, coenzymes and inorganic salts. Among the coenzymes, cozymase contains niacin as an integral component, cocarboxylase contains thiamine, while riboflavin, in the form of phosphoriboflavin-protein, enters importantly into oxidation-reduction systems. The importance of vitamins is thus shown to be at least partly derived from their participation in enzymic systems.

Yeast Respiration. Louis Pasteur, in his studies on fermentation, or "life without air," made the fundamental observation that when oxygen was admitted to the fermentation process a much more efficient utilization of the sugar resulted when expressed in terms of yeast multiplication. He drew the conclusion that fermentation was a rather wasteful process since much greater amounts of sugar were required for the synthesis of a given amount of cell substance than when the yeast was permitted to multiply in the presence of air.

The difference between the efficiencies of fermentation and "respiration," as the carbohydrate breakdown in the presence of oxygen is termed, can be readily explained when the end-products of these respective processes are considered. Fermentation, as has been seen, yields alcohol and carbon dioxide and some energy. Respiration, on the other hand, yields carbon dioxide and water, according to the following chemical equation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{much energy}$$
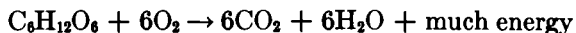
Carbon dioxide and water are what might be termed ultimate waste products, i.e., they retain no energy that is available to living organisms. The sugar has thus been oxidized to its final stage. Alcohol, on the other hand, can be further broken down, yielding the ultimate waste products carbon dioxide and water, plus additional energy, as illustrated by the following chemical equation:

$$C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2 + \text{energy}$$

In terms of calories (a calorie is defined as the unit of heat required to raise the temperature of one gram of water by 1° C., specifically from

15° to 16° C.), one mol of glucose, which is the gram equivalent of the molecular weight of the substance (180 g. in this instance) yields 674 calories upon respiration and only 27 calories upon fermentation (*84*). In other words, respiration, by bringing about the complete oxidation of glucose, produces nearly 25 times as much heat energy as does fermentation with its partial breakdown of the glucose molecule.

The inhibiting effect of oxygen upon fermentation is known as the Pasteur effect or Pasteur phenomenon. It indicates the presence in the organism of an adaptive mechanism which permits it to employ either its aerobic or anaerobic systems to obtain energy from sugar. Organisms possessing such adaptibility are called facultative organisms. In the presence of oxygen, the more efficient aerobic respiratory mechanism is employed, and the fermentation system is largely inhibited. When oxygen is lacking, the fermentative mechanism comes into play, thereby ensuring the organism's continued existence.

Yeast Manufacture. Pasteur, by showing that yeast is capable of aerobic respiration with its more efficient carbohydrate utilization, made a fundamental contribution to the economy of commercial yeast manufacture. At present, the most commonly used method for the manufacture of yeast involves the use of the molasses-ammonia process. In this process, carefully selected strains of yeast are seeded into a dilute solution of molasses, mineral salts and ammonia and permitted to grow. The solution is kept well aerated by passing sterile air through it. This aeration inhibits fermentation, as was seen above, and thereby leads to the more efficient utilization of the carbohydrate substances present in the solution. Careful control is exercised over conditions of temperature, hydrogen ion concentration, adequate ammonia and mineral supply and all other factors that affect yeast growth. After growth ceases, the yeast is separated from the exhausted solution either by filtration or centrifugation, washed, compressed and packaged in 1 pound cakes.

Active Dry Yeast. A major development in yeast manufacture came with the introduction of so-called active dry yeast shortly before World War II. Dry yeast, as its name implies, differs from common compressed yeast principally in its much lower moisture content which greatly increases its storage life and renders it less susceptible to adverse storage conditions. When kept at an average temperature of about 70° to 80° F. dry yeast retains its baking strength and activity for many weeks (*85*). Even after six months of such storage the yeast is said to produce a good loaf of bread if a slower rate of fermentation is used. If kept at a temperature of 40° F., the yeast remains viable for many months.

Dry yeast is grown much like compressed yeast. After final washing and filtration the yeast is extruded in short noodle form onto a conveyor

which passes through a dryer in which the moisture content of the yeast is reduced from some 30 percent to about 8 percent. During drying the yeast is rendered dormant and can then be transported and stored without refrigeration. Prior to its use in a dough, it requires rehydration by soaking in water at about 105° to 110° F. for five to ten minutes (*86*). The quantity of water should be about four to five times the weight of dry yeast. The fermentative action of the rehydrated yeast closely approximates that of common compressed yeast. The advantages of dry yeast have been summarized by Merritt (*86*) as follows: Dry yeast is simpler to weigh out and easier to get into suspension than wet yeast. Where fractional pounds are required it is much more accurate to weigh dry yeast than to guess at a half or a quarter of a pound of wet yeast. Dry yeast has been shown to reduce mixing time and dusting flour requirements. Deliveries can be limited to one or two a month, and the yeast need not be stored under refrigeration.

Yeast Storage. The proper storage temperature for compressed yeast in the bakery is of some importance in instances where the regular delivery of fresh yeast is interrupted for one reason or another, thereby requiring that the yeast be stored for longer periods prior to its use. Even where daily deliveries are made but the yeast is not always used on the same day, it is advisable to store the yeast at uniformly low temperatures to prevent loss of gas-producing power. As a rule, the nearer the storage temperature is to the freezing point of water, the longer can yeast be stored without marked deterioration. Thus Iwanoski and Brezezinski (*87*), cited by Baily, *et al.* (*88*), found that yeast could be stored at 32° F. for two or three months without serious deterioration. At 56° F. the safe storage limit was about two weeks and at 72° F. one week. Bailey, *et al.* (*88*) studied the effect on compressed yeast of storage for 3 months at 0°, 20°, 30°, and 45° F. Of the different storage temperatures used, they considered 30° F. as the most suitable since the yeast did not freeze at that temperature, nor lose its normal consistency. Bread made with this yeast after a two month-storage was still very satisfactory. After a three month-storage of the yeast, the loaves had a good external appearance, but an inferior crumb. The yeasts stored for the same period at the other temperatures failed to retain their original characteristics to the same extent as did the yeast stored at 30° F.; thus this latter temperature was adjudged to be the most suitable for the storage of compressed yeast.

THE MOLDS

Molds are of direct interest to the baker because they constitute a principal group of spoilage agents encountered in the bakery. Not only

are most of the ingredients used in bakery production subject to mold infection, but what is more important, the finished products themselves usually form ideal media for the growth of these fungi. In addition, several sections of the plant, such as dough rooms, proofing cabinets and bread coolers, offer a combination of moisture and temperature conditions that is highly conducive to the proliferous growth of molds which, forming large colonies, attack and weaken wooden structural portions,

FIG. 24—Striking photomicrograph showing a dense growth of mold. (*Courtesy Standard Brands Inc.*)

discolor surface paints, give rise to musty odors and in general prove highly undesirable.

As the spores of many molds are readily air-borne and are therefore easily carried by the slightest air drafts from one part of the bakery to another, the problem of keeping a bakery relatively free from fungal infections is both a formidable and a continuous one. Christensen (*89*) has shown the rapidity with which an aerial infection may spread through a building. This investigator liberated spores of a mold from a single square inch of culture surface in a room on the first floor of a four-story building. Subsequently, culture plates were exposed for five minute periods in various sections of the building. The mold organism used for this test was of a type that does not occur in air and the medium selected for the culture plates was highly specific for that particular mold so that the colonies which eventually developed on the culture dishes could

originate only from spores from the single culture surface. The results of repeated tests showed that when the spores were liberated in a room on the first floor they were carried throughout the entire building within five minutes. The conclusion is drawn that even a single slice of moldy bread, or a small quantity of moldy flour, paper, wood or debris in a bakery can readily contaminate the entire premises. The same author calls attention to previous work which showed that when a single loaf of moldy bread was brought into a room the number of mold colonies caught on culture plates exposed in the room for one minute increased from about six to more than 1000.

The Classification of Molds. The fungi are divided into four large classes, the Basidiomycetes, Phycomycetes, Ascomycetes, and Fungi Imperfecti, the chief basis for their differentiation being their mode of sexual reproduction. A preliminary distinction of two sub-groups is recognized by some mycologists on the basis of the presence or absence of cross-walls or septa in the mycelial filaments of the molds. The Phycomycetes, of which the ubiquitous bread molds *Rhizopus* and *Mucor* form the principal troublesome genera, is the only class in which the filaments or hyphae are continuous strands without septa. The class Basidiomycetes includes a varied assortment of parasitic smuts and rusts that attack wheat and other plants, as well as a picturesque array of large, fleshy fungi, such as the mushrooms, puffballs, and bracket fungi which grow upon trees. These will not be discussed further. The class of Ascomycetes is characterized by the production of ascospores in an ascus. Since yeasts possess the property of ascospore formation, they obviously belong to this class. This class also includes several familiar mold species encountered in the bakery, as the *Aspergillus* and *Penicillium* organisms. The final class of Fungi Imperfecti, which is a rather artificial class created to include all molds that are incapable of reproduction by sexual spores or in which the reproductive cycle is not completely known, includes many imperfect species of genera which primarily belong in the other classes. Examples of such species are several which form part of the *Aspergillus* and *Penicillium* genera.

The Morphology of Molds. Molds are characterized by the possession of a mycelium which is a plant body consisting of a system of fine, branching filaments or hyphae. The mycelium may be either a loose meshwork, as in bread molds, or a compact tissue as in mushrooms. Some fungi, including the majority of yeasts, do not form hyphae.

In one large class of fungi, the Phycomycetes, the mycelium lacks cross walls or septa and the entire mycelial mass forms a single cell containing many nuclei. This nonseptate structure permits the ready flow of protoplasm within the hyphae.

The other fungi possess a septate mycelium which consists of a series of individual cells attached end to end and containing one or more nuclei. In such septate mycelia the flow of protoplasm is greatly reduced. The individual cells are constituted much like the cells of yeast plants. They consist of a cell wall composed of chitin or a mixture or compound of chitin and cellulose which encloses the protoplast or cell proper. The cell may contain one or more minute nuclei. The cytoplasm is a greyish mass in which are deposited granules and vacuoles, representing reserve material of fat, protein and carbohydrate nature.

There is usually some differentiation of the mycelium into a vegetative portion and a reproductive portion. The chief function of the vegetative mycelium is to penetrate and burrow into the substrate, digesting and absorbing it. It is specialized for this work by forming little root-like processes that are of smaller caliber and more highly branched than the main mycelium. The reproductive portion usually extends up into the air, producing and discharging spores.

Reproduction in Molds. The fungi exhibit the three fundamental types of reproduction of living organisms in general. The first and simplest type does not involve specialized reproductive cells. In this so-called vegetative multiplication, a part of the ordinary vegetative body is transformed into the individual of the next generation. Thus when a small piece of mycelium is separated from the main growth, it will continue to grow independently and form a new colony by the simple process of cell division.

The second fundamental type of reproduction is by asexual spore formation. Here specialized cells are involved in the reproductive process. Usually when a fungus is a few days old it will send up numerous vertical branches, which at first are simple filaments of uniform thickness. Soon, however, a swelling appears at the tip of each branch. At first each swelling, which continues to grow into a sphere, is colorless. However, within a day or less, the sphere turns black or some other color characteristic of the mold species. This coloration is brought about by the division of the contents of the sphere into hundreds of tiny spores, each equipped with a nucleus and cytoplasm and surrounded by a colored wall. Molds generally become visible to the naked eye when they have achieved this stage. Spores which are formed endogenously within a spore case or enclosing wall are termed sporangiospores, and the spore case a sporangium. The vertical stalk which carries the sporangium is designated the sporangiophore. When the spores have attained maturity, the sporangium ruptures from internal pressure and forcibly ejects the spores, thereby aiding their distribution.

Endogenous asexual spore formation is characteristic of the Phycomy-

cetes. The other classes of fungi generally form exogenous spores, i.e., spores which are not enclosed in a spore case. In the case of these types of fungi, the vertical stalks, called conidiophores, form an enlarged globular tip from which emerges numerous small stems termed sterigmata. On the tip of these the spores, better known as conidia, are borne, usually in long chains. Discharged spores are in a state of dormancy and can retain their viability for years. When they encounter a favorable environment they germinate to produce the first filament of a new mycelium.

The third fundamental type of reproduction is sexual. While all the mold mycelia appear to be alike, there actually exists a sexual differentiation between them. Two types of mycelium are distinguished which are generally referred to as the + (plus) strain and the − (minus) strain. Neither strain can by itself initiate sexual reproduction; each requires the cooperation of the other. In the production of sexual spores adjacent filaments of the plus strain and the minus strain put out small side branches which achieve contact at their tips. A short distance behind the tip of each branch a wall is laid down transforming the tips into sexual cells or gametes. The contiguous end walls dissolve away and the two gametes fuse into one cell and constitute a zygote. This begins to enlarge and lays down about itself a heavy, dark wall. The zygote may remain dormant for months or, under the influence of warmth and moisture, it may shortly germinate, producing a vertical stalk on which sporangiospores or conidia are formed. The above account of sexual reproduction refers to the simplest form encountered, and many variations are found among different types of molds.

Typical Bakery Molds. The class of Phycomycetes contains two genera commonly encountered in bakeries as flour and bread contaminants, namely *Mucor* and *Rhizopus*, both of which belong to the family Mucoraceae. They possess a nonseptate mycelium and produce black sporangiospores. The genus *Mucor* contains many species which are quite similar to each other. One of the best known is *Mucor mucedo* which is characterized by giving rise to a coarse, woolly, whitish mycelium, whose individual filaments may attain lengths of six inches. It is often seen on decaying organic matter. Perhaps the best known of the *Rhizopus* species is *Rhizopus nigricans,* popularly referred to as "black bread mold." This species, as do all other belonging to this genus, is distinguished from the *Mucor* species by the formation of rhizoids (from which the name of the genus is derived). These are root-like appendages extending into the substance of the bread from which they draw water and organic material. The rhizoids also give rise to the sporangiophores. The mold spreads rapidly over the surface by sending out stolons or runners

much in the manner of strawberry plants. These runners take hold of the substrate by forming rhizoids for penetration into the bread substance and the production of sporangiophores. The mycelium is at first white, but later turns brown. The sporangiophores generally occur in clusters of three, five or more. The mold contains a high content of amylases and proteolytic enzymes. These enable it to thrive on starchy media of higher moisture content, such as bread and other baked products.
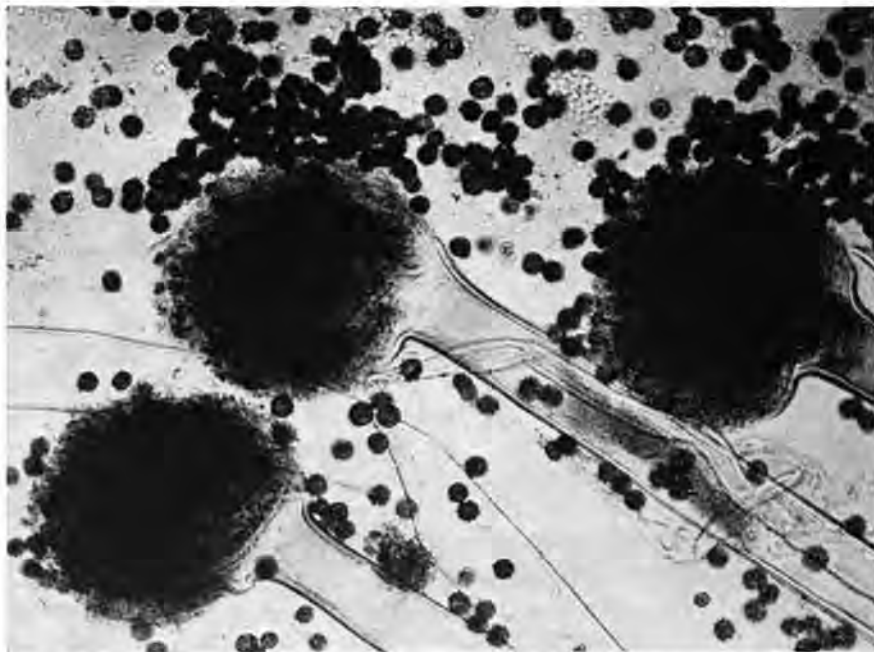
Fig. 25—*Rhizopus nigricans*—a dense black fungus. (*Microphotograph by M. Toch.*)

Most of the genera of the class Ascomycetes, which include specific bakery molds, are encountered in their conidial forms among the Fungi Imperfecti, so that it may prove more convenient to discuss them as members of the latter group. Among these genera may be included *Aspergillus, Penicillium, Oidium* and *Monilia*.

The Aspergilli form septate mycelia and may be recognized by the characteristic arrangement of their conidia and conidiophores. The vertical unbranched stalk arises from an enlarged, so-called foot cell of the vegetative mycelium. On its upper end the stalk has a bulbous swelling from which protrude several sterigmata which, in turn, carry chains of conidia, giving the entire structure a globular brush-like appearance. Species of aspergilli which are frequently encountered in bakeries include

Aspergillus glaucus which forms green or grey-green conidia, and *Aspergillus niger* which forms large round masses of black conidia and is for this reason sometimes confused with *Rhizopus nigricans.*

The Penicillia, like the Aspergilli, possess mycelia which are septate in structure. They also produce conidia from sterigmata in clusters which in their form are suggestive of a brush. Various species differ in the color and form of their conidia. *Penicillium* species occurring in old

Fig. 26—*Aspergillus niger*—a mold which infects bread. (*Microphotograph by M. Toch.*)

bread may be usually recognized by their light blue or green color. Recently *Penicillium* species have assumed outstanding importance as the source material of the therapeutic antibiotic substance Penicillin which is produced by the species *Penicillium notatum* and *Penicillium chrysogenum.*

Oidium and *Monilia* are organisms which are intermediary between the yeasts and the molds, being usually classed with the latter, however. Their intermediary position arises from the fact that although they generally produce a mycelium, they are also able to exist in an unicellular state and to produce by budding as do the yeasts. A typical *Oidium* species is *Oidium lactis,* commonly encountered in soured milk and other

dairy products. A representative of the genus *Monilia* is *Monilia sito-phila* (more recently renamed *Neurospora sitophila*). This species usually forms a loose network of mycelia which, after conidia are formed, turn orange and salmon-red in color. The organism has been identified as a harmful mold causing occasional epidemics of infected bakery goods.
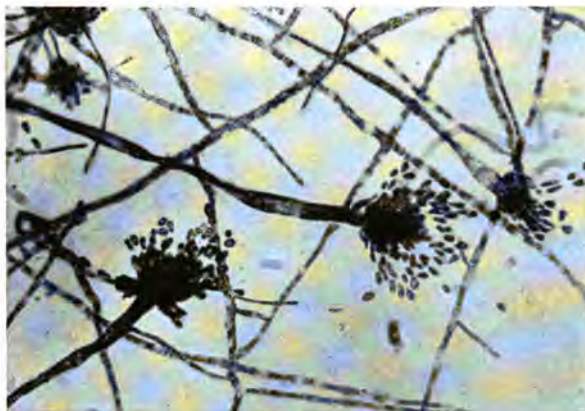
FIG. 27—*Green Penicillium,* a common bread mold. (*Microphotograph by M. Toch.*)

Its spores are unusually resistant to heat, being able to withstand exposures up to 248° F. for thirty minutes in a dry state.

BACTERIA

Most biologists consider bacteria to be plants, largely on account of their apparent similarity to the blue-green algae, the simplest and most primitive of plants. Accordingly, bacteria belong to the class of the *Schizomycetes,* a sub-group of the thallophytes. All bacteria are unicellular organisms whose only method of reproduction is by simple cell division, or fission. Their rate of reproduction is tremendously high, some bacteria growing to maturity and dividing every twenty minutes under favorable conditions. Many of the bacteria tend to form colonies, most commonly of the filamentous type. They all possess rather generalized protoplasm, with no clear differentiation of nucleus, vacuoles, etc., as is found in yeast and mold cells. Many bacteria, however, contain granules which stain more intensely than does the rest of the cell. The suggestion has been advanced that some of the granules consist of chromatin, which is a form of protoplasm believed to represent the most vital and fundamentally essential part of living matter, and actually constitute nuclei or nucleus-like collections of protoplasm (*90*). For the most part the granules appear to represent reserve food substances, such as starch or glycogen or fat. Many bacteria possess extremely fine whip-

like extensions, called flagella, which endow them with motility in liquid media. Spherical bacteria generally do not show flagellation and are therefore as a rule non-motile.

Bacteria are presumed to be the smallest known living organisms, some species being on the borderline of visibility under our best microscopes. They range in size from about 0.5 micron in diameter to about 1 micron in length in the case of cylindrical forms, although certain species attain lengths of 200 to 500 microns.

Some bacteria secrete around themselves a mucilaginous coat which is referred to as a capsule. The conditions under which capsules are formed, the chemical composition of capsules and the relation of capsules to the cell all vary with different species. In some cases, capsules seem to result from a thickening of the outer cell membrane, while in others the organism appears to secrete a mucoid substance which adheres to the cell. Frequently the capsular material is quite viscous and if a large colony of growing bacteria is touched by an object, a slimy, thread-like connection results when the object is withdrawn. The organism responsible for ropy bread produces such capsular material.

 Types of Bacteria. Three general forms of bacteria are differentiated according to the shape of their cells: (1) round or spherical cells known as the "coccus" form; (2) rod-shaped cells known as the "bacillus" form; and (3) banana or cork-screw shaped cells referred to as the "spirillum" form.

The spherical cells are found to occur in various combinations, such as

> isolated single cells called monococci or cocci
> paired cells called diplococci
> chain formations called streptococci
> massed bunches called staphylococci
> cubical packets called sarcina

The rod-shaped cells, or bacilli, are also divided into two general groups depending on their ability or inability to form spores. The nonspore-forming bacilli are called Bacteria (with a capital initial to differentiate them from the name of the whole group of single-celled organisms which is spelled with a lower case initial). The spore-forming organisms are referred to as the bacilli (singular, bacillus). The spore formation of a bacillus has nothing to do with reproduction, as is the case with yeasts and molds, but is merely a means for assuming a dormant condition under certain conditions. Sporulation is not necessarily a response to unfavorable conditions, since spores are often formed in young cultures even when conditions are otherwise highly favorable. In sporulation, the protoplasm of the cell rounds up more compactly and usually surrounds

itself with a thick wall. In this state the organism becomes dormant, i.e., it reduces its life activities to a practically imperceptible rate. Bacterial spores show a greatly increased resistance to heat, drought, cold, sunlight and chemical disinfectants which is thought to be due to some kind of dehydration of the protoplasmic protein within the spore. Sporulation thus permits bacteria to survive conditions in which the active, vegetative organism would soon perish. To obtain complete sterilization, there must be boiling under pressure, or the thorough application of disinfectants to every spot where bacteria might be present.

Spiral- or corkscrew-shaped cells may appear as (1) short rigid spirals, (2) long rigid cells, and (3) long flexible cells. Many of them are also capable of spore formation and the vegetative cells are frequently equipped with cilia or flagella.

Bacterial activity accounts for the major part of the decomposition of animal and plant matter that occurs in nature. This decomposition, or decay, is accomplished by means of bacterial enzymes which break down the carbohydrates, fats and proteins which constitute the organic matter.

Growth Requirements of Bacteria. The rate of bacterial activity is closely associated with bacterial growth. Hence factors governing the growth of bacteria are important also in their control. Bacterial growth is affected by moisture, temperature, food supply, pH of the medium, presence of antiseptics and disinfectants, high concentrations of sugar and salt, oxygen supply, and light.

Most bakery raw materials are protected from bacterial spoilage by their relatively low moisture content. When, however, such materials as flour, powdered eggs, milk powder, etc., are allowed to become damp, the danger of putrefaction or decay is materially increased.

As in the case of yeast, bacteria possess maximum, minimum, and optimum temperatures. Growth ceases on freezing, but the bacteria may remain viable for long periods of time. For the vegetative cell, the maximum survival temperature in most instances is in the vicinity of 150° F., while for the spores it is much higher. Spores may be effectively destroyed by heating to 250° F. under pressure for 20 minutes. Optimum temperatures for growth of bacteria vary widely with different species. Many bacteria which occur in the soil, water, air or animal bodies grow well at temperatures between 77° and 104° F. Species growing well in this temperature range are called mesophilic, which means moderation-loving. Some soil and water bacteria grow best at temperatures only little above freezing and these are referred to as psychrophilic (cold-loving), while some species grow best at temperatures from 140° to 175° F. and are called thermophilic (heat-loving).

Bacteria thrive best at a pH near neutrality or only slightly on the

alkaline side; a few exceptions, such as the lactic acid and acetic acid bacteria, are acid-producing organisms. In general, a pH value within the range of 6.5 to 8.0 will prove most conducive to bacterial growth.

Certain chemicals exert either an inhibitory or outright destructive effect on bacteria. They are generally referred to as antiseptics and disinfectants. Though these terms are frequently used interchangeably, an antiseptic is a substance that stops bacterial growth without necessarily
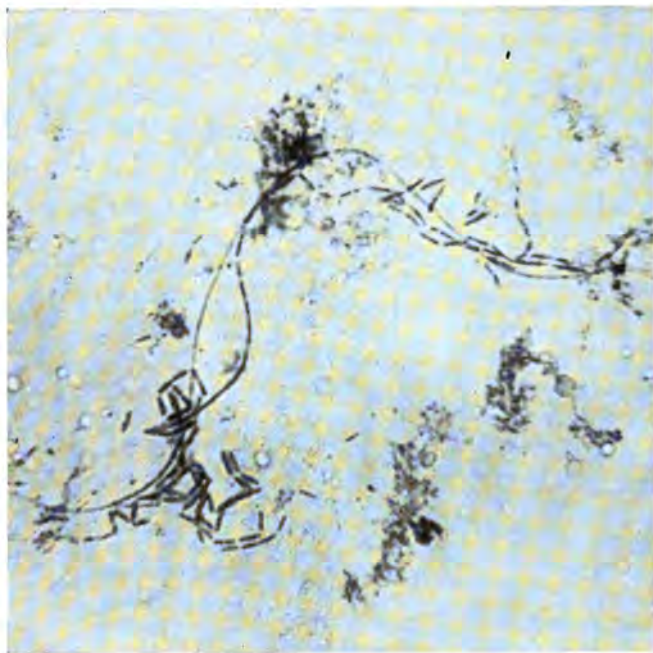
FIG. 28—Rope bacteria in their vegetative state (highly magnified).

destroying the bacteria, whereas a disinfectant is a bacterial killing agent. A chemical which is antiseptic in effect when in dilute solution may become a disinfectant at higher concentrations. Examples of such chemicals are formaldehyde, alcohol, carbolic acid, strong acids, and hydroxides.

Media which contain high concentrations of sugar or salt will not support bacterial growth, though certain other microorganisms, such as molds, may grow in them satisfactorily. This is explained by the fact that the high concentration of sugar or salt in the environmental medium, associated with the low concentration of these substances in the cell fluids, induces a movement of water from the cell interior outward leading to a loss of moisture in the cells: this proves fatal to the organism.

With regard to their oxygen requirement, bacteria may be divided into

three distinct groups, namely those which grow only in the presence of oxygen and which are called *aerobes*, those which thrive only in the absence of oxygen and which are called *anaerobes*, and those which can adapt themselves to both the presence or the absence of oxygen and are termed *facultative anaerobes*.

Ropy Bread.   Although the baker should have a general interest in the bacteria as a group, there are two organisms which are of special concern to him.   The first of these is the bacillus responsible for the condition known as rope in bread.
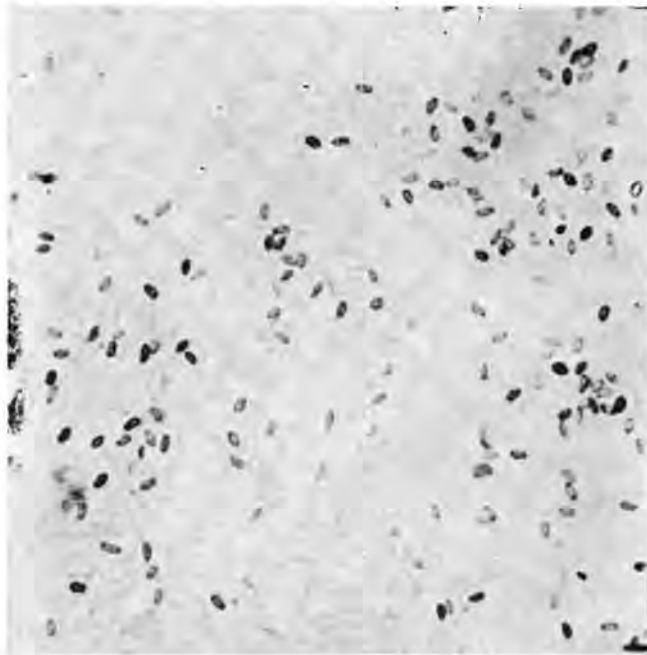
Fig. 29—Rope spores (highly magnified).

Bacteriologists are now generally agreed that the causative agent of ropy bread is the *Bacillus mesentericus*, which in earlier literature was designated by such names as *Bacillus mesentericus vulgatus*, *Bacillus mesentericus viscus*, and *Bacillus panificans*.   The reason for this multiplicity of names is due partly to the fact that different investigators have independently studied and named the organism.

A bacillus has been earlier defined as a rod-shaped organism capable of forming a highly resistant spore.   It has also been pointed out that some bacilli secrete a mucilageous covering or capsule.   Both sporulation and capsule formation occur in the rope-producing bacillus and account for the characteristics of ropy bread.

Baking temperature will destroy those bacilli present in their vegetative or growing state. These temperatures, which seldom exceed 210° F. in the loaf interior, are however insufficient to kill the spores of the bacillus. After bread cooling, the spores revert into the vegetative state and being in a favorable medium begin to multiply at a prodigious rate. The bacteria secrete enzymes which break down the proteins of the bread. They also produce the slimy capsules which, when the bread is pulled apart, form the fine silky threads frequently observed. The spoiling
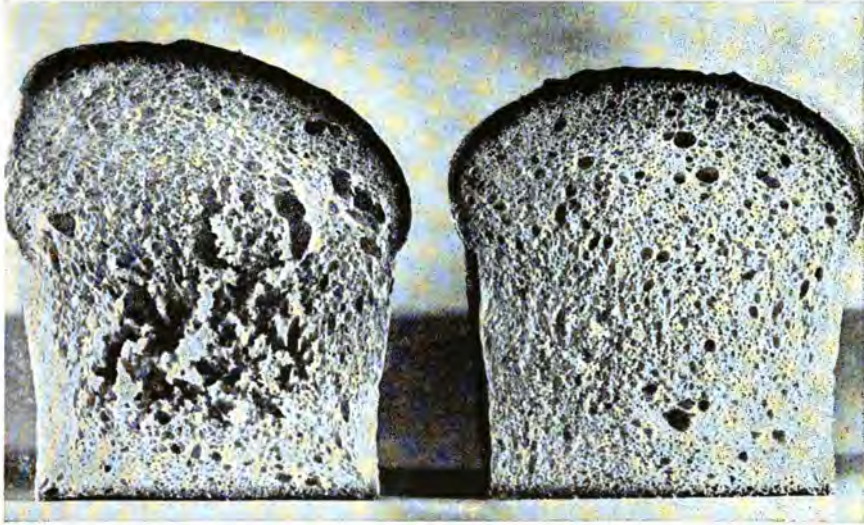
Fig. 30—Rope infection shown in loaf at left, results in crumb discoloration and cell break-down. (*Courtesy Standard Brands, Inc.*)

bread will take on the characteristic ropy odor suggestive of an over-ripe cantaloupe and the bread interior will become soft and sticky with a brown discoloration. Ropy bread occurs most frequently in the summer season when the climate is warm and humid.

Since the atmosphere is replete with bacteria and bacterial spores, it is practically impossible to prevent the access of harmful bacteria to the bakery. Furthermore, nearly every ingredient used by the baker contains rope-causing bacilli. Under present commercial practices, the main sources of infection are flour, yeast, and malt, with flour being by far the leading offender. Sources of infection may also develop within the bakery in cracks and crevices of troughs, mixers, and other machinery which may harbor these bacilli waiting for more favorable growth conditions.

Bleeding Bread. The second specific bacterium of special interest to bakers is *Micrococcus prodigiosus* (or *Serratia marcescens*), the organism

which on occasion causes red spots to appear in bread. This condition is at times also referred to as "bleeding bread." The causative organism is a small coccus of low heat resistance which will not withstand baking temperatures. Infection thus takes place after baking. Growth occurs in the form of patches which are at first colorless but which eventually develop a blood-red tint. It may proceed to a stage where dripping results due to the digestion of the bread by the enzymes of the bacteria. Thus the name "blood rain" has also been applied to this condition. These bacteria are far less common than the rope bacilli and an infection by them is readily eradicated by a thorough cleaning and disinfection of the plant.

Food Poisoning. Any discussion of bacteria would be incomplete without a brief reference to the problem presented by occasional outbreaks of bacteria-induced food poisoning. This subject is of special importance to bakers since it is not unusual for bakery products to be suspected as the cause of such outbreaks whether the facts warrant such suspicion or not. Bacterial food poisoning may be attributed to one of two causes (*91*): the food ingested may be contaminated with living bacteria which cause illness in man, or the food may contain toxins produced by bacteria. *Salmonella* and *Streptococcus faecalis* are the most common causative agents of the former type of food poisoning, while staphylococcal food poisoning is caused by toxins.

The *Salmonella*, or paratyphoid, groups of bacteria include some 200 individually recognized kinds of microorganisms, ranging from the ordinary colon bacillus to the highly dangerous typhoid bacillus. The source of these organisms is usually traceable to contamination of food with bacteria from the intestinal tracts of men or animals. The majority of *Salmonella* infections cause acute gastro-intestinal disorders, the symptoms generally being abdominal cramps, diarrhea and, in some instances, vomiting. The period of incubation, i.e., the period which elapses after ingestion of the contaminated food and the onset of the illness, ranges from a minimum of 7 to 8 hours to a maximum of 72 hours, with the average being between 12 to 24 hours. In addition to other foods, bakery products have been incriminated at one time or another in *Salmonella* food infections.

The second common type of bacterial food infection involves *Streptococcus faecalis*, which is a normal inhabitant of the intestinal tract of man and animal. This food poisoning results in a relatively mild illness of short duration with symptoms of abdominal cramps, diarrhea and occasionally vomiting. The incubation period is usually between 7 to 15 hours.

The most frequent food poisoning, the so-called staphylococcal food

poisoning, is caused by a toxin produced by staphylococci during their growth in the food. The bacteria themselves, when freed from the toxic material, have been shown to be harmless. The symptoms of staphylococcal food poisoning commonly begin within an hour or so after ingestion of the contaminated food. They include violent nausea and vomiting, prostration, and severe general malaise. The disease is seldom fatal and usually of short duration. Baked goods have occasionally been incriminated in outbreaks of staphylococcal food poisoning.

According to Cathcart (*92*), practically the only bakery products implicated in food illness outbreaks are cream-filled products. The number of outbreaks generally increases during summer months when temperature conditions favor frequency of infection, rate of microbial multiplication and degree of virulence. *Salmonella* and staphylococci are quite ubiquitous and may readily infect bakery products by means of impure ingredients, contaminated water, unclean utensils, air currents, etc. Proper refrigeration of fillings and of the finished products is an important safeguard, but is not completely reliable since, if infection is present, the bacteria merely become dormant at the low temperatures only to resume their active growth as soon as the temperature is raised to a suitable level. A far better procedure is to pasteurize the cream-filled products by exposing them subsequent to filling to temperatures of 375° to 425° F. for a period of 30 minutes. Gilcreas and Coleman (*93*) have found that staphylococci in custard filling in éclair shells were rendered nonviable by a much less severe treatment, heating for only 15 minutes at only 216-220° F. being found sufficient for this purpose. No impairment of appearance or palatability of éclairs, chocolate cream pie and Boston cream pie resulted from re-baking these pastries for 20 minutes at 216° F. Pasteurization should be carried out as soon as possible after filling to prevent prior growth of staphylococci bacteria since the toxin elaborated by these organisms remains unaffected by the heat treatment. Tests by Cathcart (*92*) have shown that certain fruit fillings have an inhibitory effect on the growth of bacteria. In the descending order of their effectiveness, these fruits are lemon, pineapple and orange. It is recommended, therefore, that during the summer months at least, pure fruit fillings, instead of plain custard, be made whenever possible.

CONTROL OF BREAD INFECTIONS

Mold and rope infections of baked products have in the past caused annual losses amounting to millions of dollars. Although modern methods of control have greatly reduced the incidence of bread infection, the problem is still short of its complete solution. While strict adherence to sanitary principles tends to reduce the severity of mold and rope out-

breaks, it cannot prevent them entirely, especially when high summer temperatures and humidities combine to create conditions favorable to growth of these organisms. This follows from the fact that the normal atmosphere within a baking plant cannot be sufficiently controlled, even by the application of air-conditioning, to eliminate the presence of mold and bacterial spores. Since these spores occur in the atmosphere in all sections of the bakery, bread out of the oven is subject to infection as soon as its surface cools to a temperature below the thermal death point of mold. The rate of infection is surprisingly high. Thus Dennington (*94*) cites the survey results obtained by G. H. Gilmore of the Mellon Institute which indicate that in the wrapping room of an average bakery mold spores settle from the atmosphere at an approximate rate of 700 per hour per square foot area. In the cooling room the rate averages 420 mold spores. Bread from the oven is sterile with respect to mold since the temperatures attained during baking exceed the thermal death point of mold. This, however, does not hold true of the rope bacilli which are far more heat resistant. Hence, if rope infected ingredients are used in the production of baked products, this infection will persist beyond the point of baking, even though no further infection does occur.

The baker has several means at his disposal for the control of bread infections. One is by increasing the acidity of the medium, i.e., the baked product, to a point where it will either no longer support or greatly retard the growth of mold and rope organisms. The use of vinegar has been very popular in the past for this purpose. More recently, however, it has been observed that vinegar exerts also a specific toxic effect upon these microorganisms which suggested a second method of control, namely the use of specific inhibitors. A third method aims at a reduction of the incidence of infection by elimination of the organisms from the atmosphere by germicidal ultra-violet radiation provided by special lamps. A final method, little used as yet, is that of destroying mold spores present in sliced wrapped bread by exposure of the product to rapid high frequency heating with the aid of special dielectric units.

Kirbey, Frey and Atkins (*95*) have studied the influence of acidity upon the growth of *Aspergillus niger*. They found that this mold has no sharply defined growth optimum with respect to the initial pH of the medium, but grows equally well between pH values of 3.5 to 6.0, provided no acids of specific toxic effect are present. Acetic acid was found to have a marked toxicity for this mold, the active agent being the undissociated acetic acid molecule and not the acetate ion. Furthermore, it was observed that the lower the initial pH value of the medium containing the acid, the greater was the acid's disinfecting and retarding action. In a continuation of these investigations, five typical bread molds representing those fre-

quently found on bread were studied (*96*). These molds included *Aspergillus niger, A. fumigatus, Neurospora sitophila, Rhizopus nigricans,* and a green mold isolated from a loaf of commercial bread. The results indicated that in addition to acidity, the specific effect of the kind of acid used is of great importance upon mold growth. The effect of different acids at the same pH level may vary considerably. As a rule, fatty acids are much more toxic to molds than are mineral acids and such organic acids as lactic, citric, tartaric, and malic. Acetic acid, in the form of vinegar, has a very marked influence on the growth of bread molds. Similar activity is shown by formic, propionic and butyric acids. The effect of acetic acid at a fixed concentration was shown to be a function of the pH of the medium. At pH value of 5.5 to 6.0, such as occur in commercial bread, acetic acid retards the initial growth of the molds studied, but was found to have only a slight effect on the ultimate growth of these molds.

· The discovery of the fact that certain lower fatty acids exert a definite toxic effect upon molds and rope organisms led to their use as the active ingredients of commercial mold and rope inhibitors. Glabe (*97*) has listed the following requirements for mold and rope inhibitors: (a) They must be effective at low concentrations without noticeably affecting the pH of the product; (b) they must be nontoxic and harmless in concentrations considerably in excess of normal usage; (c) they must not produce deleterious effects upon the dough and bread characteristics; (d) they must not present a problem in handling during the production process; and (e) they must be inexpensive to use. At present, three salts of the lower fatty acids are most extensively used. They are sodium diacetate ($NaC_2H_3O_2 \cdot HC_2H_3O_2 \cdot \frac{1}{2}H_2O$), described by Glabe (*97*), and calcium propionate and sodium propionate, which have been discussed by Miller (*98*). These substances are marketed under different trade-names in the form of white salts and are highly effective inhibitors. One-third percent of either of the propionates (approximately 5 oz. per 100 lbs. of flour) or 0.4 percent of the acetate (approximately 7 oz. per 100 lbs. of flour) will inhibit completely the development of mold and rope for ten days or longer in hot, humid weather. Normally, 2.5 to 3.5 oz. per 100 lbs. of flour will provide adequate protection. Calcium propionate should not be used in cake batters since the calcium tends to react with the baking powder ingredients. For these types of doughs the sodium salts are recommended.

Bacillus mesentericus is far more sensitive to high acidity than are the molds. In contrast to the latter, the growth of *B. mesentericus* is completely inhibited at a pH of 4.6, and greatly retarded at pH levels of 5.0-5.2. This pH range is therefore relatively safe for baked products providing the rope contamination is not heavy. A common method of safeguarding against the occurrence of rope has been to aim at somewhat

lower than normal pH values in the finished product. This may be accomplished by a vigorous fermentation and a slightly greater dough maturity, or by the addition of small amounts of calcium acid phosphate or of vinegar to the dough. These substances, while they lower the pH of the bread, also exert a specific toxic action on the rope organism. The maximum amounts of these substances normally used are 1 pint of vinegar per 100 lbs. of flour or 12 oz. of calcium acid phosphate on the same flour basis. In recent years, the use of these two rope inhibitors has declined in favor of the acetate and propionate salts.

Kuehl (*99*) has suggested the use of lactic acid in concentrations of the order of 0.5 percent as a rope inhibitor. This acid is said to be effective not only as an inhibitor but also as a bread improver since it exerts a growth stimulating action on yeast. The same author suggests the following simple method for the detection of rope infections in flour and similar materials: Fifty grams of flour or milled product are added to 75 cc. of distilled water in an Erlenmeyer flask and the flask plugged with cotton. It is then placed in a water bath and heated for 15 minutes at a temperature of 212° F., during which time all heat-sensitive bacteria will be destroyed. The flask is then stored at a temperature of 86° to 95° F. If after 24 hours the characteristic odor of rope is detectable it is an unmistakable sign that infection is present.

In addition to chemical mold inhibitors, another means of combatting the mold problem is by the elimination or reduction of the incidence of infection by the use of germicidal ultra-violet rays (*100, 101*). Whereas mold inhibitors attempt to render molds already present on or in the baked product innocuous by preventing or retarding their active growth, the germicidal rays of ultra-violet lamps act to reduce the degree of infection by sterilizing the atmosphere to which the baked products are exposed from the time they are baked until they are sealed in their protective wrappers. Germicidal irradiation does not give absolute mold protection and has little practical effect on rope infection. It does, however, extend the mold-free life of baked goods beyond the time for which such products are normally kept.

Clark (*102*) has recently summarized a number of recommended practices designed to reduce the incidence of rope and mold infection. Principal among the suggested procedures is an efficiently organized program of plant sanitation covering such major points as periodic washing down of walls, floors and ceilings, followed by the application of sterilizing solutions; cleaning and sterilization of equipment; cleaning of water supply tanks and pipe lines, flour bins, conveyors, etc.; use of clean covered containers for ingredients; and avoidance of nesting of containers in which ingredients are weighed and handled. In addition to cleanliness, other

suggestions made by Clark are: (a) storage of raw materials in cool, properly ventilated and well-illuminated storage rooms; (b) vigorous and healthy fermenting at normal temperature and with a proper amount of yeast which will depress the pH of the dough and thereby make it less conducive to rope development; (c) thorough baking which, although it does not destroy rope spores, will retard rope development because of a decreased moisture content of the loaf; (d) thorough cooling of bread, preferably in an atmosphere of washed or filtered air; interior of bread should be 90° F. or lower before slicing and wrapping; (e) washing or filtering the air entering the bakery to eliminate dust particles which carry rope and mold spores; (f) preventing entry into the plant of stale baked products; (g) maintaining bread boxes, delivery trucks and store storage in a clean, cool and well-ventilated condition. These precautions will go far in preventing serious outbreaks of rope and mold infections, although under extremely unfavorable conditions they may still prove inadequate.

CHAPTER VII

ASPECTS OF PHYSICAL CHEMISTRY

Since all ingredients used in baking, with the possible exception of such purely crystalline substances as salt and sugar, exhibit colloidal behavior which greatly affects their function during the various stages of the baking process, it will prove desirable to discuss briefly and in a very elementary fashion a few concepts of colloid chemistry which have a more or less direct bearing on baking.

COLLOID CHEMISTRY

Definition of Colloid Chemistry. Colloid chemistry has variously been defined as "the physical and chemical behavior of extremely minute particles in relation to their surroundings" (*11*) and as dealing with "particles which are so small that they behave in some respects like molecules, and with molecules so large that they behave in some respects like particles" (*103*). Colloids may thus be considered as very finely divided matter or as very large molecules. The units of measurement in colloid chemistry are the micron, whose symbol is μ, and the millimicron, or $m\mu$. One micron is equivalent to 1/1000th of a millimeter or 1/25,000th of an inch, while one millimicron is one millionth of a millimeter. The smallest particle visible to the unaided eye is about 1/250th of an inch or, expressed in metric units, 100 microns in diameter. A good compound microscope has a resolving power about 200 times that of the human eye so that particles as small as 1/50,000th of an inch, or 0.5 micron, in diameter can be distinguished. The particle size embraced by colloid chemistry begins at its upper range where the microscopic level stops, namely at about 0.5 microns, or 500 millimicrons, and ends at about 1 millimicron, which very nearly brings the smallest colloidal particle down to the size of inorganic molecules. Depending upon the configuration of the particle, extensions in one or two dimensions up to 5 microns may still keep the particle within the colloidal size if the other dimension is correspondingly small, as is the case with fibrillar and laminar particles.

The smaller a particle, the larger is its surface in relation to its mass. Hence a greater proportion of the molecules constituting a particle will be found to lie at the surface in a minute fragment of matter than in a larger one. At the colloidal level surfaces exert a tremendous influence upon the

chemical and physical behavior of particles since an appreciable fraction of the molecules lies at surfaces, rendering them highly reactive in proportion to the mass of the matter involved.

Surfaces exist only at the interfaces or boundaries between two phases or states of matter. There are three states of matter—gas, liquid and solid. Our most common experience pertains to the interface between solids and gas; thus the everyday objects we see and handle appear to us as finite because they exhibit interfaces, or surfaces, which delimit their forms in relation to the gaseous atmosphere, i.e., solid and gas form an interface.

States of Matter. It may not be inappropriate at this point to digress somewhat and consider some of the basic properties of the three states of matter. Solids are characterized as having rigidity of both form and volume. In other words, the atoms and molecules of a solid occupy fixed positions with relation to each other, the attractive forces binding them together being strong enough to overcome almost completely their kinetic energy. Liquids have rigidity of volume but not of form. Hence in a liquid, while the distances between the molecules are fixed, the relative positions of the molecules are not. The individual molecules constantly move past each other in rapid, irregular motion, a fact that explains the formation of homogeneous solutions in which the molecules of the dissolved substance diffuse rapidly and uniformly throughout the volume of the solvent. Gases have neither rigidity of volume or of form. Here both the distances and the positions of the molecules relative to each other are constantly changing.

If we view an atom or a molecule as a field of force, it will be seen that in a solid or liquid a molecule located at the surface will not have the same molecular environment as a molecule located within a particle or liquid. An interior molecule or atom will be entirely surrounded by other molecules or atoms which exert upon it equal attractive forces from all sides, thereby establishing a balance or equilibrium. A molecule at the surface of a liquid or solid is not in the same state of balance. It will have attractive forces exerted upon it from five directions, but there is no force acting on it from the sixth direction. Hence its own attractive force remains partially unsatisfied since there is always at least one side where no corresponding opposite force exists. This condition is responsible for many physical as well as chemical properties of liquids and solids. Thus the adsorptive character of solids, i.e., their ability to attract and tenaciously hold certain liquids and gases on their surfaces, is due to this unsatisfied attractive force which exists at their interface.

Not all substances will attract each other with equal strength. The degree of mutual attraction between different types of molecules depends to

a considerable extent upon their similarity of size and shape. Other factors are also involved. The more closely the molecules of two different substances fit together, the more points of contact will exist between their atoms or ionic groups, and the greater will be the attractive force. Thus if water is spread over a greasy or oily surface, it will not spread but collect in small, spherical droplets. The explanation for this phenomenon is that the molecules of the fat or oil are so much greater than, and so vastly different from, the molecules of water, that very few points of contact are formed and the points of attraction actually established between the water molecules and the fat molecules are by far inadequate to overcome the attractive forces existing between the water molecules themselves. The spherical shape assumed by the water droplets is a demonstration of its surface tension, a property possessed by liquids in general. It is the direct result of the unbalanced attractive forces exerted upon the liquid's surface molecules. Since the surface molecules are pulled toward the interior with greater force than in any other direction, and since there is no outward pull at all, the surface of the liquid will tend to grow smaller. An isolated body of liquid has a minimum surface area when it is a sphere and this accounts for the common observation that small drops of liquids are spherical.

If, on the other hand, water is spread upon a perfectly clean glass, metal, wood or other surface from which all traces of fat have been removed, the water film will remain in a distended form. In other words, the attractive forces between the molecules of the solid and of the water are either equal to or greater than the attraction which exists between the water molecules. The strong attraction of such solids as the proteins for water accounts for the swelling or hydration of these substances when they come in contact with water under suitable conditions. The water penetrates into the interstices formed by the large protein molecules and forms layers of films upon the interstitial surfaces, causing them to separate and thereby increasing the volume of the particles.

Colloidal Systems. Colloidal systems constitute mixtures of at least two different phases of matter. If the three states of matter are combined two at a time, nine possible systems are produced. Since, however, a mixture of gases is always a single gaseous phase, it being impossible to create an interface between two different gases, only eight colloidal disperse systems are encountered. These are given in Table 27.

In the above list of colloidal systems it will be noted that in every case the phases are divided into continuous and dispersed. While this holds true in most systems, it is not always necessary to have one of the phases dispersed in the other. Thus it is quite possible to have a mixture of two continuous solid phases "just as two continuous nets of different yarns

may be interwoven." Wet gluten is an example of a continuous solid and a continuous liquid phase. There also exist so-called mixed systems in which all three phases of matter are present. Flour dough represents such a system in which the gluten strands and the water films constitute continuous solid and liquid phases, respectively, while the finely dispersed gas cells are present in the discontinuous or dispersed phase.

A colloidal system in which solid particles are dispersed in a liquid is referred to as a sol, to distinguish it from a true solution. In true solutions

TABLE 27. TYPES OF HETEROGENEOUS DISPERSION

Dispersed phase	Continuous phase	Examples of Colloidal Systems
Gas	Liquid	Foam
Gas	Solid	Solid foam or porous solids, bread
Liquid	Gas	Mist, fog
Liquid	Liquid	Emulsions, e.g., milk
Liquid	Solid	Jellies
Solid	Gas	Smoke
Solid	Liquid	Suspensions
Solid	Solid	Colored glass and precious stones

the dispersion of the solute is on the molecular level, i.e., the dissolved substance separates into individual molecules or ions which disperse homogeneously throughout the volume of the solvent. Thus when sugar is dissolved in water, a clear solution is obtained in which the individual sugar molecules cannot be detected by any available physical means. When a protein, such as gelatin, is dissolved in water, a clear solution or sol is also obtained. However, the individual protein particles are of sufficient size to become distinguishable from the solvent when subjected to such refined testing methods as the ultramicroscope, X-ray diffraction, ultracentrifugation and others. Sols resemble liquids in their main physical properties, i.e., they flow and do not show rigidity of form. When a sol assumes a rigid form, it is referred to as a gel. Thus a solution of gelatin, when cooled, becomes a translucent, elastic gel.

A sol or gel in which there is strong attraction between the colloidal particle and the solvent is characterized as "lyophilic" which means "attracting the liquid." Another common term for such a system is "emulsoid." On the other hand, systems in which the particles have no affinity

for the molecules of liquid are called "lyophobic" meaning "liquid repelling." The corresponding alternate term for such systems is "suspensoid."

Suspensoids owe their stability mainly to the fact that they carry an electric charge due either to ionic adsorption on their surfaces or to their partial ionization in solution. Since the particles will carry the same charge, either negative or positive, they repel each other and hence do not form larger aggregates. It is obvious that the addition to such a system of any electrolyte that will neutralize the charge on the colloidal particles (i.e., any common salt, acid or base) will tend to reduce its stability and, if sufficient electrolyte is added, the colloidal particles will unite into larger aggregates which settle out of solution as a precipitate. The resultant sediment can no longer be redispersed into the solvent to reform a colloidal system.

Emulsoids owe their stability to their great affinity for the dispersion liquid. This generally implies that the dispersed particles undergo considerable swelling. Thus when gluten particles are placed into very dilute acids, they will be observed to disintegrate slowly. The water molecules penetrate between the protein molecules and pry them apart, causing the particles to swell. As this process continues, the individual large protein molecules are completely surrounded by water molecules and become detached from the original particles, resulting eventually in a colloidal solution. Protein molecules contain both weak acid and basic groups, so that they ionize slightly in water, thereby assuming an electric charge. The way in which ionization proceeds is greatly influenced by the concentration of acid or alkali present in the solution, i.e., by the pH of the dispersion medium. A protein molecule may thus carry either a predominantly positive or negative charge depending upon the pH conditions it encounters. This charge aids in the stabilization of the sol similar to the stabilizing effect of the electric charge mentioned in the case of lyophobic sols. It is possible, however, to select conditions under which the protein molecules dissociate equally as acids and as bases and hence have no charge, i.e., the solution is at the isoelectric point. At this point the sol shows its minimum stability. In contrast to lyophobic sols, however, the lyophilic sol still retains some stability and precipitation does not necessarily follow when the isoelectric point is reached. Addition of electrolytes far in excess of the amount required to precipitate a lyophobic sol will also coagulate a lyophilic sol, the action in the main being one of dehydration, i.e., the withdrawal of water from the colloidal particles by the electrolyte.

The sols considered thus far possess the principal property of a liquid, namely, the ability to flow under the action of the smallest force. It is possible, however, in many of the systems to increase the amount of the

dispersed solids to a point where rigidity of the system results so that small forces cause only elastic deformation. In most cases flow can be initiated only after a critical stress, called the "yield value" is surpassed. A great number of different types of gels exist which vary widely in their properties. In the case of gelatin dissolved in hot water and permitted to set on cooling to a clear jelly, the rigidity of the system is attributed to the long molecular protein chains which possess rather strong interacting forces and hence form an interlocking three-dimensional network providing structural support for the water molecules which quantitatively far exceed the protein molecules. A gel can thus be formed when only two percent of gelatin is added to water. Pastes, which are plastic masses containing a high proportion of colloidal solid constituent, are closely related to gels.

Emulsions. A true emulsion represents a colloidal dispersion of one liquid in another when both liquids are mutually immiscible. Emulsions are of two main types, oil in water, and water in oil. In the absence of an emulsifying agent such emulsions show only limited stability. The two liquids tend to separate, with the oil droplets coalescing to form larger droplets which rise to the surface and form a separate layer. It is possible, however, to stabilize an emulsion by the addition of a suitable substance which is termed an emulsifier. The function of an emulsifier is to reduce the interfacial tension existing between the water and the oil, thereby making them mutually less repellent. Oils, being long hydrocarbon chains, are non-polar and have no pronounced electrical properties. They also have a comparatively low interfacial tension and therefore spread more easily than water. The water molecule, on the other hand, is strongly polar. Since this is the case, the addition of a substance possessing both polar and non-polar characteristics to an oil in water emulsion should act to reduce the interfacial tension. Among substances possessing such a dual character are the fatty acids. A molecule of a fatty acid consists of a long hydrocarbon chain or tail, constituting its non-polar portion, and a COOH group or head, constituting its polar portion. The hydrocarbon chain is soluble in oil, whereas the polar head is soluble in water. Thus when a fatty acid is added to an oil in water emulsion, the fatty acid will coat each particle of oil. The polar head will ionize, thereby losing a hydrogen ion and becoming negatively charged. It is thereby attracted to the positive portion of the water molecules and will hence orient itself in such a manner that the hydrocarbon tail is submerged in the oil particle, while the polar head rests in the surrounding water. This molecular film or skin thus forms a link between the discontinuous phase and the continuous phase. Since the negative polar heads form the outer surface of the suspended oil particle, the particle as

a whole will show a negative charge toward its environment and hence also owes its stability to an electric charge just as has been found to be the case above with suspensoids and emulsoids. Emulsifying properties are not limited to fatty acids, but are possessed by higher alcohols, phospholipids, gums and by proteins. Thus the emulsifying action of egg white is due to its albumin, while that of egg yolk is attributable to its phospholipids. Even so-called stable emulsions may be readily broken down by any means which disrupt the protective interfacial film. Thus milk is an emulsion of butter fat in a solution of proteins, milk sugar and salts. The protective protein film around the fat particles may be broken and coagulated by agitation, thereby enabling the fat particles to stick together. This fact is utilized when the cream is churned in the production of butter.

Emulsions may also be stabilized by a process known as homogenization in which the usually variable size of the dispersed fat globules is greatly reduced to a more or less uniform diameter by the application of considerable force. Homogenization greatly alters the properties of the original natural emulsion, such as milk, for example. Thus, whereas raw milk creams readily on standing, it is difficult to separate cream from homogenized milk even by centrifugation. Homogenized milk cannot be churned into butter and homogenized cream does not readily whip into a foam. There is a considerable increase in viscosity of the homogenized products. All these changes are due to the subdivision of the naturally occurring fat globules into smaller particles, whose number may thereby increase a thousandfold, with a correspondingly great increase in adsorptive surface. There occurs, as a result, a much greater adsorption of milk proteins by the fat globules.

Foams consist of more or less stable liquid-air interfaces, the air cells or bubbles being surrounded by liquid films which constitute the continuous phase. Although the individual air or gas bubbles are usually large enough to be visible to the naked eye, foams are counted among colloidal systems because they require stabilizers of colloidal size to give them some permanence, pure liquids being unable to form a foam. In baking the most familiar examples of foam are beaten egg white and whipped cream. Aerated cake batters and fermented doughs may also be considered as special types of foam, although in the latter case the continuous phase possesses characteristics which are the attributes more of solids than of liquids. The foaming properties of liquids depend upon the viscosity of the liquids, which should exceed a certain degree, and a low air-liquid surface tension. In egg white, whipping not only incorporates air but also causes an adsorption of proteins at the air-water interface which imparts structural strength to the cell walls and at the same time

reduces the surface tension. The addition of acid to egg white increases foam stability, whereas the presence of egg yolk reduces it. In whipped cream the stability is also attributable to the cell-like structure of the air bubbles. The protein adsorbed at the air-liquid interface stiffens on denaturation and further strength is imparted by the presence of the partially solidified butter fat. The cream's whipping capacity is increased by aging, and by high fat and nonfat solids contents. Homogenization largely destroys a cream's whipping capacity.

The reader will find more detailed discussions, both theoretical and practical, in the works of Alexander (*104*), Dean (*103*), Ward (*105*), Hawley (*106*) and others.

THE COLLOIDAL STRUCTURE OF DOUGH

When flour and water are mixed together, the finely granulated milled product is changed into a mass possessing elastic, viscous and plastic properties. These are the results of the colloidal structure of the dough.
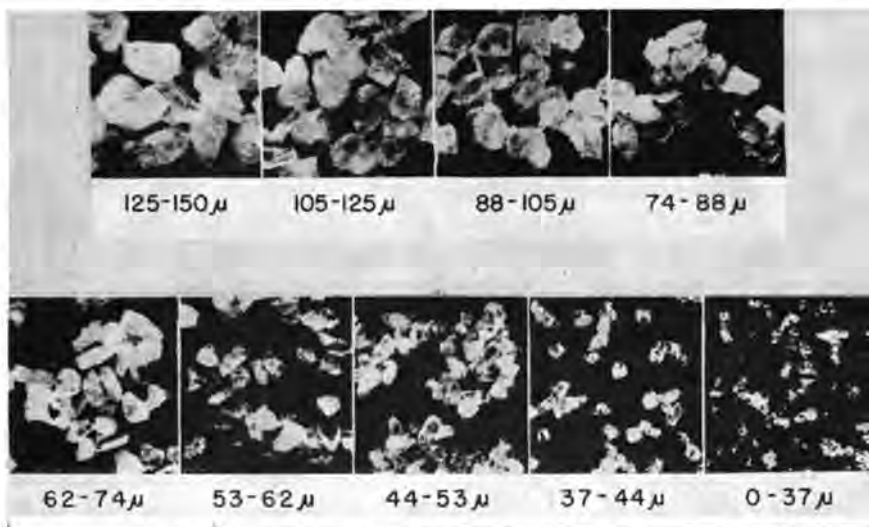
FIG. 31—Photomicrographs of flour particle size fractions. (*Courtesy Kansas State College.*)

In order to form a partial concept of the factors which govern dough behavior it is necessary to have some understanding of the individual elements which contribute to the formation of the dough. In the following paragraphs an attempt will be made to summarize rather briefly our present knowledge of the interrelation of protein, starch and water, the main constituents of dough.

The individual flour particle is an extremely fine fragment of the wheat endosperm consisting essentially of starch and protein, the former being about six times as large in quantity as the latter. Flour particles vary considerably in size, ranging in a straight grade flour from 0 to 150 microns. Wichser and Shellenberger (*107*) have separated straight grade flours into several well-defined particle size groups and determined the percent of each fraction with the results shown in Table 28.

TABLE 28.   PERCENT OF PARTICLE SIZE FRACTION EXISTING IN FLOUR

Fraction Particle size	Amount of each fraction	
	Hard Red Winter Flour	Hard Red Spring Flour
Micron	%	%
105-150	8.3	14.5
88-105	10.0	13.5
74-88	12.5	13.5
62-74	13.5	13.0
53-62	10.4	10.5
· 44-53	10.1	9.0
37-44	7.8	7.0
0-37	27.2	19.0

The starch present in these flour particles occurs in the form of granules. Bailey and Grewe (*108*) have made measurements on starch granules of 17 flours and found that 81.6% of the total number of granules had a diameter of less than 7.4 microns, 12.5 more than 14.8 microns, while the remaining 5.9% ranged between these two sizes. Thus the granules of wheat starch fall into rather distinct size groups, the one and by far the major group consisting of the relatively small granules of less than 7.4 microns in diameter, and the other comprising the relatively large granules of over 14.8 microns. The average granule diameter appears to be around 5 microns.

The granule, however, is still not the smallest starch unit since it in turn consists of individual starch molecules whose average size has been estimated to be of the order of 5 millimicrons, or 1/1000 the diameter of an average wheat starch granule. The composition and general characteristics of starch are discussed in some detail in another chapter on The CARBOHYDRATES.

The second major components of flour particles are the wheat proteins which in the endosperm of the wheat kernel form the matrix in which the starch is embedded. This protein material is separable by the use of proper solvents into at least four distinct fractions: glutenin, gliadin,

edestin and leucosin. The two principal fractions are glutenin and gliadin which, when wetted, form the gluten of the dough. The proteins in general and the wheat flour proteins in particular form the subject matter of a separate chapter to which the reader is referred for a more detailed discussion.

Wichser and Shellenberger (*107*) have shown that a remarkable degree of variation exists in the protein content of the various size groups of flour particles. In the case of the hard red winter wheat, the fraction of 105-150 microns particle size had a protein content of somewhat less than 10%. The protein content increased progressively with a decrease in the size of the flour particle to nearly 14% in the 37-44 micron fraction. The corresponding protein contents for these two fractions of hard red spring wheat flour were slightly over 11% and nearly 15%, the latter values in both cases being at a level well above that of the control flours. The fraction of 0-37 microns constituting the finest particle size was found to consist largely of free starch granules and of the dry finely-divided protein material. The same authors also found a similar, though less pronounced trend in the ash content of the different particle size fractions, the ash content increasing progressively with a decrease in the size of the flour particle. These findings indicate that the endosperm in wheats is non-uniform in chemical or physical composition, varying by zones from the center of the endosperm to its outer edge.

When flour is mixed with water, the first physical action of basic importance which occurs is the wetting of the flour particles. Wetting involves the phenomenon of adsorption in which two substances exert mutually attractive forces which causes one of the substances to adhere to the other's surface. Water wets flour particles because it is attracted to the starch granules and protein material. Since adsorption, by definition, is a surface phenomenon it is apparent that the amount of surface exposed will have a predominant quantitative influence upon the adsorptive powers being effected. The relative increase in surface area which results with a decrease in particle size is truly phenomenal and may be illustrated by the following example. A cube measuring 1 centimeter along each edge will have a surface area of 6 cm². If that cube is now subdivided into cubes measuring one-tenth centimeter along each edge, a total of 1000 such small cubes are obtained from the original cube and their total surface will be 1000 x 6 mm² or 60 cm². There has thus been a tenfold increase in the surface area, accompanied by a corresponding increase in adsorptive power, although the original mass has remained unchanged. Repeating the division by the same extent, i.e., into cubes having edges measuring one-tenth mm. (which is equivalent to 100 microns), a total of 1,000,000 cubes will result. The surface area in this case will then be

600 cm². Since the size of flour particles is within the range of 37 to 150 microns, one cubic centimeter will contain approximately one million flour particles whose total surface is thus truly enormous in comparison with their volume. Furthermore, whereas the starch granules present a fairly uniform surface, this is not true of the protein particles whose surface is highly irregular and therefore still larger in relation to the mass. The fact that protein possesses a larger adsorptive power than starch finds at least a partial explanation in this irregularity of surface.

Free and Bound Water. The adsorptive power of colloids, such as are represented by the flour starch and protein, acts to bind molecular layers of water so tightly to their surfaces that this adsorbed water, also called bound water, may well be considered a part of the starch or protein particle since it is not available for solvent action. As more and more layers of water molecules are adsorbed and superimposed upon each other, those molecules which are farther removed from the adsorbing surface are less and less strongly held until a level is reached when it is difficult to decide whether a layer of water is to be considered bound or free. In other words, there is no strict demarcation between bound and free water in the dough. According to Swanson (*31*) it is the water in the dough which remains unadsorbed that imparts to dough the properties designated as plastic and viscous, and the depth of adsorbed water films which mostly determine whether the dough has the desired consistency.

A brief explanation of the terms adsorption and absorption might not be out of order at this point. According to Glasstone (*109*) "The term adsorption refers strictly to the existence of a higher concentration of any particular component at the surface of a liquid or solid phase than is present in the bulk." Adsorption thus refers to a surface characteristic of substances which enables them to attract and hold unto their surfaces other substances by means of forces which can be of chemical, electrical, thermal, or other nature. Adsorption is not limited to any particular state of matter but may occur between solids as when fine dusts cling to solid surfaces, between liquids as when oil films spread on wet pavements, between solids and liquids as when water wets solid surfaces, between solids and gases as when charcoal retains gas molecules, etc. Absorption, on the other hand, designates a condition where there is a "more or less uniform penetration of the adsorbed substance into the interior of a solid or a liquid" (*31*). From what has been said above, absorption in the case of a dough may to a large extent be designated as adsorption, at least insofar as the bound water is concerned, with only a part being absorbed in the exact sense of the term, i.e., held by capillary forces.

The manner in which water is distributed in dough has been studied by a number of investigators. While there is general agreement that part of

the dough water occurs in a free state and part in a bound state, estimates as to how much of the water is bound have varied from 35.5 percent determined by Vail and Bailey (*110*) to some 82 percent found by earlier investigators. The wide discrepancy in values obtained is explained by Swanson (*31*) on the basis that since there is no sharp line of demarcation between free and bound water, differences in the method of measurement are apt to yield rather divergent values. The subject has recently been subjected to another investigation by Baker, Parker and Mize (*111*). These authors define bound water as that portion which "combines with the flour constituents to form hydrates, or is bound by polar groups or otherwise reacted in such manner that it is no longer available as a solvent." They determined the water-binding capacities of starch and gluten separately by exposing purified samples to the vapor of supercentrifugates previously obtained from doughs. Dry flour was shown by this method to bind 27.3 percent of its weight of water. Vail and Bailey (*110*), using a quite different method, had found the hydration capacity of flour to be 28.6 percent when calculated as bound water held per unit weight of dry matter. There is thus rather close agreement between these two values. Baker and his co-workers further calculated the volumes occupied by the solution containing solubles and by the hydrated insolubles, gluten and starch, in a dough of 72 percent absorption and arrived at the following values: 47.0 percent of the dough volume was aqueous solution, 44.2 percent hydrated starch, and 8.8 percent hydrated gluten. The hydrated gluten and the aqueous solution are closely associated and move together in dough around the starch. This mixture of dough liquid, comprising 55.8 percent of the dough volume, contributes fluid and elastic qualities to the dough while the starch imparts puttylike properties to the dough.

When water is first added to flour, the water does not penetrate into the flour but forms a fine dough film at the interface or boundary line between the water and the flour. It requires the action of the mixer arms to break up this dough film and expose new flour surfaces to the water. As the mixer arms continue to bring about new contacts of water with flour, eventually films of water will surround and penetrate into each flour particle to be held there by adsorptive and capillary forces.

Whereas no actual absorption of water by starch granules occurs at the temperatures at which dough mixing is normally carried out, an apparently chemical union occurs between water and the protein material leading to the formation of a three-dimensional network of very fine strands (*112*). As mixing is continued the gluten strands or fibrils are stretched and rearranged into a parallel pattern which is evidenced by the dough assuming an increasing smoothness. At the same time the gluten fibrils are criss-crossed and wound about starch granules producing a honey-

comb effect of minute cells filled with starch granules and air incorporated into the dough during the mixing operation. The dough at this point has reached its minimum mobility. Mixing beyond this stage results in stretching of the gluten fibrils beyond their elastic limits and there may be either an excessive thinning of the fibrils or their actual breaking into shorter filaments. They thereby lose their strength and the dough, which is now over-mixed, becomes sticky and runny.

Dough as a Plastic Mass. The physical properties of dough are derived primarily from a combination of the characteristics of two states of matter, namely liquid and solid. If we take as a distinguishing characteristic between solids and liquids the fact that the former have a definite shape whereas the latter have no shape of their own but assume the shape of the containing vessel, then dough can be considered neither a true solid nor a true liquid, but as possessing properties associated with both states of matter. One characteristic of solids is that their shape can be deformed by the application of sufficient force. Because of the elastic nature of solids, the deformation, if it does not exceed a certain magnitude, will disappear again when the deforming force is removed. This phenomenon can readily be observed on dough which springs back after a deforming pressure is removed. The dough therefore behaves like an elastic solid. On the other hand, when a dough ball is left to stand for a period, it slowly loses its spherical shape and flattens out. In this case it exhibits the property of flow that is characteristic of liquids.

Halton and Scott Blair (*114*) explain that the peculiar internal structure of dough accounts for the combination of the elastic properties of a solid with the viscous properties of a liquid. They view flour dough as containing protein chains which behave like "coiled springs" and which are responsible for its elastic behavior. The linkages between these protein chains are not, however, equally strong at all points so that when the dough is extended some of them break almost immediately, causing permanent deformation or flow, while others remain intact and maintain the rigid structure of the dough. "All these adjustments in the protein network have to take place in the presence of a starch-water mixture which, although primarily fluid, also possesses some rigid properties, thus complicating the situation, and making impossible the complete relaxation of even those protein units which are capable of truly elastic recovery."

The various theories and experimental observations have been summarized by Swanson (*113*) who gives them an interpretation somewhat as follows: Elasticity is usually associated with solids in which the molecules are held in fixed positions by surrounding forces. The degree of elasticity inherent in a solid substance is governed by the extent to which the molecules may be moved from their position without a permanent break. In

some instances, such as steel, this elastic limit is small, whereas in others, such as rubber, it is large. Dough has an elastic limit of about 30 percent. The cause of elasticity in dough is explained by the theory advanced by Halton and Scott Blair. During dough mixing, the protein particles, which are assumed to be springlike structures, are arranged more and more into a parallel system, a condition which is revealed by the familiar smoothness of a properly mixed dough. At this stage of mixing, the dough exhibits maximum resistance to pulling and the greatest degree of elasticity because at this point the greatest number of gluten "coils" are in position to resist elongation on the one hand, and to spring back after elongation, on the other. Mixing beyond this stage breaks down the dough by causing the rupture of weaker spring elements first, followed by slippage of the stronger gluten coils past each other and their eventual breaking. Breaks of the links of these springs result in nonrecoverable deformation, in other words, plastic deformation. Since the elastic character of the dough inheres principally in its gluten, whereas the quantitatively predominating starch fraction contributes primarily plastic properties, dough as a whole possesses a higher degree of plasticity than of elasticity. In addition dough exhibits also viscous properties which are associated mainly with the water films present within the dough. As the elastic elements are embedded in these films, the three physical properties of elasticity, plasticity and viscosity are thus closely associated and must be studied more or less together.

The Origin of Gas Cells in Dough. Ordinary dough is never a completely compact mass but is always subject to some degree of aeration. Although the gas cells in dough, whether incorporated during mixing or created during fermentation and subsequent manipulation, are far too large to fall within the category of colloidal aspects of dough, they occupy an exceedingly important position with regard to the physical structure of dough and are indirectly related to its colloidal nature insofar as the principal endeavor of the baker is to so control the colloidal properties as to yield an optimum cell structure within the dough and bread. It may, therefore, not be inappropriate at this point to consider briefly the origin and general structure of the gas cells in dough.

The origin and structure of gas cells in dough has been studied chiefly by Baker and co-workers. With regard to the origin of gas cells, Baker and Mize (115) have investigated the relative significance of five hypothetical sources of gas cells in dough. These are enumerated as follows:

1. The gas cells in the endosperm particles are incorporated in the dough.
2. The gas voids between the endosperm particles are incorporated in the dough.
3. The mixing beats gas into the dough and subdivides it to produce gas cells of small size.

4. The gas pressure caused by yeast will originate new gas cells around the organism.
5. The work applied to the dough after it is mixed, such as folding, punching, rolling, moulding and twisting, subdivides gas particles to increase their number.

By mixing doughs in vacuum and subjecting them to high pressure, each hypothetical source was studied with a minimum of interference from the other variables. The results obtained indicate that the yeast organism is incapable of originating gas cells in dough (source 4). The gas generated by the yeast organism diffuses into pre-existing gas cells without creation of further cells. These pre-existing cells occupy about 8 percent of the dough volume and are produced in mixing. It was further shown that the gases entrained in the endosperm (source 1) or occluded in the flour (source 2) or beaten in during the early stage of mixing are of little or no consequence as a source of gas cells in a properly developed dough. Premixing the doughs in a vacuum and then giving them a brief mixing in air showed that the latter portion of the mixing period is capable of emulsifying or occluding all of the required gas to initiate the resulting gas cells which produce texture in bread. In this connection, a subsequent study by the same authors (*116*) of the rate of gas incorporation or occlusion during various stages of dough mixing (by means of comparing the density of dough obtained at successive mixing intervals with that of gas-free dough) showed that gas incorporation did not proceed at an even rate during mixing but that it was slow at the beginning and most rapid at the point when the dough offered its greatest resistance to mixing. The best bread is obtained just prior to the point of most rapid gas occlusion. This is interpreted as indicating that the fine cell structure of bread is not obtained by gas occlusion but rather by the subdivision of gas cells during the subsequent steps of the baking process, such as punching, moulding, rounding, etc. These steps, while they do not incorporate new gas cells into the dough, create a greatly increased number of cells by subdividing those already present, and further develop the gluten and tend to render it airtight so that the gas cells retain their integrity. Comparison of the cell structure of doughs and baked bread shows that all of the cells found in bread exist in the dough when placed in the baking pan. The differences that do exist in the bread texture as compared to the aerated dough are attributable to the coalescence and breaking of the cells during moulding, proofing, and baking.

The role of oxidation in the development of texture is principally one of imparting proper strength and extensibility to the cell walls. Unoxidized or green doughs will incorporate as much air as will properly oxidized doughs. However, the former lack the strength to prevent coalescence of gas cells during proofing and baking so that a rather coarse

bread texture results, whereas the latter doughs are able to retain their fine cell structure. On the other hand, over-oxidized doughs possess a tough gluten structure which is unable to withstand the severe action of punching and moulding without breaking the gas cells and giving rise to a coarser texture.

Structure of Individual Cells. The structure of individual gas cells was studied by Baker (*117*). He was able, by carefully diluting properly oxidized dough with brine, to separate intact gas cells in the form of thin, translucent protein bubbles which could be studied for their properties. The material of the cell walls was shown to be essentially glutinous in character, containing approximately 45 percent protein and 55 percent fine starch on the anhydrous basis. When the bubbly material was placed in a vacuum chamber the cells expanded to 10 times their original volume without rupture. Observations made on doughs fermenting in glass jars, where the interior surface of gas cells is visible, showed that the walls of bubbles from unoxidized doughs are dull in appearance in contrast to the shiny and smooth walls present in oxidized doughs. Upon large expansion of the dough, transparent cell walls made their appearance in which the wall material is practically free from starch. Apparently there is a tendency of gluten to draw away from the starch during fermentation, indicating that starch is not necessarily required for cell formation. This view is further supported by the dull appearance of bread crumb made from unoxidized dough on the one hand, and the sheen or very shiny appearance which characterizes the crumb of quality bread. In the former case, the cell walls appear to contain considerable starch which roughens the surface, whereas in the case of the properly oxidized doughs gluten is drawn into the surface of the cell wall and gives it a shiny appearance. The thin film of gluten lining the surface of gas cells presumably contributes greatly to their gas-tight properties and strength. Baker suggests "that this film is drawn to the surface because the gas nucleus from which the bubble originated started in a glutinous core. As the bubble was expanding the required amount of gluten to satisfy its surface needs was drawn from the starch-gluten matrix of the endosperm material. The properties that enabled this to occur may be controlled by the viscosity and fluidity of the gluten and by the amount of adhesion of the gluten to starch."

The beneficial effects obtained from punching are attributed to the collapsing of such glutinous cell surfaces which thereby provide new glutinous centers in which the entrapped gas nuclei can develop with subsequent tighter gluten walls. Dough development during mixing has been shown to be due principally to the stretching and folding action of the

mixer. The stretching operation is thought to draw the gluten from the endosperm particle matrix to the surface of the particle and produce there a gluten concentrate which is then available for holding gas nuclei incorporated in the mixing.

A somewhat different view with regard to the origin of gas cells is held by Burhans and Clapp (*118*), based on observations made during a microscopic study of dough during various stages of mixing, fermentation, and baking. They found that while the yeast cells do not form the foci of gas cells, as would ordinarily be assumed, the fermentative action of yeast is largely responsible for the origin and formation of the cell structure of dough and bread. They observed that the carbon dioxide produced by yeast diffuses into the aqueous suspension surrounding the yeast cell, where at first it remains in solution. As more carbon dioxide is formed, the vapor pressure of the gas in solution increases until in areas between several yeast cells a weak point in the gluten matrix gives way and a gas pocket forms. Continued carbon dioxide production enlarges existing gas bubbles by diffusion and the resulting tension raises the vapor pressure to form others.

After dough fermentation, the action of heat during baking produces alterations of the minute dough structures. Oven spring results, first, from faster gas production, second, from further extension of the cell structure subsequent to both the softening of the gluten by heat and plasticization of the starch, and third, from the rapid appearance of numerous new bubbles in the walls of the pre-existing ones. The rise in temperature has several effects upon aeration of the dough. As the temperature increases, the carbon dioxide is rendered less soluble so that more gas comes out of solution. Furthermore, heat causes the gas to expand. During the initial period of baking there is also an increased production of gas due to the accelerating effect of moderately high temperatures upon yeast enzymes. All these factors combine to greatly increase the gas pressure within the loaf. As the gluten softens and the starch becomes plastic, this increased gas pressure results in a marked distension of the existing cells and the formation of new ones in the gluten matrix. Increased extensibility is evidenced by the remarkable thinness of the bubble walls and of the gluten strands, while plasticity of the starch is shown by its conformity and elongation as part of the walls. Further rise in the temperature slows and finally inactivates zymase at about 60° C., but coagulation of the gluten is probably well under way. The still higher temperature rise, besides releasing dissolved gases, effects vaporization of alcohol, organic acids and water, and so replaces fermentation to a degree. Terminally, the coagulation and gelatinization become complete and permanently fix the structures.

HYDROGEN ION CONCENTRATION

One of the most significant chemical theories is that of electrolytic dissociation. According to this theory, all acids, bases and salts dissociate or break up into positively and negatively charged atoms and molecules, called ions, when dissolved in water or other suitable solvent. Because solutions of ionizable substances are good conductors of electricity, such substances are known as electrolytes or polar compounds. Thus, highly purified water is a very poor conductor. If, however, sodium chloride (NaCl) is added to the water, the resultant solution becomes an excellent electrical conductor. On the other hand, if sugar were added to such water, its conductivity would remain unchanged. Hence salt is classified as an electrolyte, whereas sugar is a nonelectrolyte.

The reason why aqueous solutions of salts, acids and bases are good conductors of electricity is found in the presence of electrically charged ions. Common table salt does not occur in solution to any extent in the form of NaCl molecules, but rather as individual Na ions carrying one unit of positive electrical charge (indicated as Na^+) and individual Cl ions carrying a corresponding unit of negative electrical charge (indicated as Cl^-). Sodium chloride hence dissociates as follows:

$$NaCl \leftrightarrows Na^+ + Cl^-$$

The possession of an electrical charge by an ion greatly alters its properties as compared with the corresponding element in its neutral state. Sodium chloride consists of only sodium and chlorine. Chlorine in its elemental state is a yellowish, highly corrosive gas with a pronounced odor, while sodium is a soft grey metal that reacts explosively with water. If table salt were to dissociate into its respective atoms when put into solution, one would expect entirely different results than are actually obtained. Hence the logical assumption is that it dissociates into ions with properties different from those of the respective elements.

It may be readily shown that electrolytic dissociation of polar compounds does actually occur in solution by inserting two electrodes connected to a storage battery into a solution of, for example, hydrogen chloride, which is hydrochloric acid. When the circuit is closed one of the electrodes becomes positively charged and is called the anode and the other becomes negatively charged and is called the cathode. Bubbles of gas will be observed to form at both electrodes. Suitable methods of analysis will show that the gas at the anode is chlorine, while that at the cathode is hydrogen. Their evolution results from the fact that the respective ions are neutralized upon contact with the oppositely charged electrodes. That is, the chloride ions travel toward the anode and give

up their extra electron, while the hydrogen ions travel toward the cathode and take on their lost electron. For this reason negative ions are called anions, while positive ions are termed cations. A hydrogen ion, having lost its charge, becomes an atom and immediately unites with another hydrogen atom to form molecular hydrogen, which is a gas. An analogous transformation occurs with chloride ions which, upon neutralization, form molecular chlorine.

Electrolytes may be either strong or weak, depending upon the degree of their dissociation in solution. Such compounds as hydrochloric acid, sodium chloride, and potassium hydroxide, etc., are strong electrolytes because they ionize almost completely, that is, solutions of these compounds do not contain very large proportions of them in their molecular form. With weak electrolytes, such as acetic acid, sodium acetate and ammonium hydroxide, ionic dissociation occurs to a far lesser degree. Since in the case of acids, and for that matter also of bases, reactivity is synonymous with the degree of ionization, a solution containing a given amount of a highly ionizable electrolyte is therefore much more reactive than a solution containing an equivalent amount of a slightly ionizable electrolyte.

This relationship between strength or reactivity and degree of ionization becomes more readily apparent when it is realized that the properties of acids are principally derived from their formation of hydrogen ion in solution, and those of bases or alkalies from their formation of hydroxyl ion in solution. Strong acids exhibit their acidic character to a marked degree because they provide more hydrogen ion through their more complete dissociation, whereas weak acids, because of their less extensive ionization, show their acid character to a reduced degree. In the case of bases, an analogous situation is encountered. Here the alkaline character is derived from the presence of hydroxyl (OH^-) ions. Strong bases, being more completely ionized, provide more hydroxyl ions, while weak bases, being less ionized, provide fewer hydroxyl ions. The actual strength of a given solution thus depends upon two factors—its concentration in terms of quantity or amount of acid or base present, and the degree of ionization. Concentration is determined by titration, while reactivity is measured by determining the solution's hydrogen ion concentration.

Titration: Titration is a laboratory procedure for determining the amount of a substance in solution by the addition of measured amounts of a standard neutralizing solution in the presence of an indicator to show the end point when neutralization is attained. Standard solutions of acids or alkalies are based on so-called normal (N) solutions which contain a gram equivalent weight of the solute per liter of solution. The gram equivalent weight of a compound is its molecular weight in grams

divided by the total valence of the positive ions or radicals present. Thus the molecular weight of hydrogen chloride (HCl) is 36.5. Since it contains one hydrogen ion with a valence of 1, its equivalent weight is also 36.5, so that a normal solution contains 36.5 grams of the compound in one liter of solution. Sulfuric acid (H_2SO_4) has a molecular weight of 98. However, it contains two hydrogen ions, each with a valence of 1. Therefore its molecular weight is divided by 2 to arrive at its equivalent weight. Hence a normal solution of sulfuric acid contains 49 grams of the compound in one liter of solution. With acids containing three hydrogen ions, such as phosphoric acid (H_3PO_4), the molecular weight must be divided by 3 to arrive at the equivalent weight. In the case of alkalies, in which the positive ion is usually a metal, the same logic applies. Thus in sodium hydroxide (NaOH) the cation is the sodium ion with a valence of 1, so that the molecular weight of 40 is also the equivalent weight of its normal solution. Barium hydroxide ($Ba(OH)_2$), on the other hand, has a positive ion with a valence of 2, hence its molecular weight, which is 171.4, must be divided by 2 to yield an equivalent weight of 85.7 for its normal solution.

The great advantage of normal solutions is that equal volumes of an acid and of a base will exactly neutralize each other, the hydrogen ions supplied by the acid uniting with the hydroxyl ions of the base to form water, and the positive ion of the base uniting with the negative ion of the acid to form the corresponding salt, according to the following example:

$$NaOH + HCl \rightarrow NaCl + HOH$$
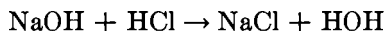
Normal solutions should be distinguished from *molar* (M) solutions, which latter contain one gram molecular weight of the compound per liter of the solution. From this definition it is apparent that in the case of acids and bases in which a single positive ion has a valence of 1, normal and molar solutions are identical. However, in cases where the positive ions have a valence of two or more, or where the compound contains two or more monovalent cations, the respective normal solutions will have only one half or one third or less the amount of solute as compared to molar solutions. Since molar solutions may vary in the amount of available hydrogen or hydroxyl ions, equal amounts of molar solutions of an acid and an alkali do not necessarily neutralize each other. For example, when 10 cc. of a molar solution of sodium hydroxide (NaOH) are added to 10 cc. of a molar solution of sulfuric acid (H_2SO_4), neutrality is not attained since the H_2SO_4 will provide twice as many hydrogen ions than the number of hydroxyl ions supplied by NaOH, so that an excess of H ions will remain after reaction and the solution will show acidic char-

acteristics. A normal solution of sulfuric acid, on the other hand, would contain only half the amount of acid per unit volume and hence would be exactly neutralized by the same amount of normal sodium hydroxide solution.

In titration a commonly used indicator is phenolphthalein, which is colorless in an acid or neutral solution and pink to red in an alkaline medium. In carrying out a titration, an exact amount of the unknown solution is taken and a few drops of phenolphthalein added, which reveals by its color reaction whether the solution is an acid or an alkali. If it is an acid, a standard solution of alkali, which may be either normal, 0.5N, 0.1N, or any other convenient but known strength, is used as the titrating solution. If the unknown sample is an alkali, a standard acid solution is used. The titrating solution is slowly added from a graduated burette to the sample until a change in indicator color shows that neutrality is attained. From the amount of titrating solution required to reach neutrality, and knowing its concentration, the amount of solute present in the measured amount of the sample may be easily calculated.

Active Acidity. While titration reveals the concentration of a solute, whether acid or base, in solution, it does not give information of the reactivity of the solution. Thus equivalent amounts of hydrochloric acid (HCl) and acetic acid ($HC_2H_3O_2$) would require the same amount of sodium hydroxide to neutralize each, yet there exists a marked difference in their reactivity. This becomes readily apparent from the following example. To prepare normal solutions of hydrochloric acid and acetic acid, respectively, one would need to add 36.5 grams of hydrogen chloride in one case and 60 grams of acetic acid in the other to enough water to make up one liter each. Each of these solutions would thus contain 1 gram of ionizable hydrogen. The degree of ionization in the two cases, however, is vastly different. At normal concentration, acetic acid ionizes to an extent of 0.4 percent, whereas hydrochloric acid may be considered to ionize 100 percent. Thus in the former case only 0.4 percent of hydrogen is present in the form of hydrogen ion, whereas in the latter case all of the hydrogen is present in ionized form. The actual quantity of hydrogen ion present in 1 liter of normal solution of acetic acid is therefore:

$$1 \times \frac{0.4}{100} = 0.004 = 0.4 \times 10^{-2} \text{ g. of hydrogen ion.}$$

In the case of the hydrochloric acid one liter of normal solution will have 1 gram of hydrogen ion. Thus, although both solutions contain the same amount of hydrogen and are therefore equivalent in total acidity as determined by titration, the hydrochloric acid contains about 250 times as much hydrogen ion as does the acetic acid solution. Hence as far as active acidity is concerned, the former is 250 times stronger than the latter. It

is apparent, therefore, that to determine the amount of active acid or active alkali present in a solution, a type of measurement different from titration must be employed.

It has been stated above that highly purified water is a very poor conductor of electricity. This statement is only apparently in conflict with the practical observation that moisture and an electrically charged wire form an extremely dangerous combination since actually natural waters are never pure. Even distilled water will normally contain some dissolved carbon dioxide gas (CO_2), taken up from the air, which combines with the water molecules to form carbonic acid (H_2CO_3) as follows:

$$CO_2 + H_2O \leftrightarrows H_2CO_3$$
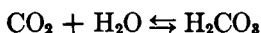
It is, however, possible under highly exacting laboratory conditions to prepare absolutely pure water which is then found to be a very weak conductor of electricity. Water, hence, dissociates only very slightly into hydrogen ions and hydroxyl ions according to the equation:

$$HOH \leftrightarrows H^+ + OH^-$$

and may for all practical purposes be considered as nonionized or to occur in its molecular form. By means of highly refined methods it has been shown that the degree of dissociation of pure water results in a concentration of hydrogen ions and of hydroxyl ions equivalent to 1/10,000,000 of a mole each per liter. A mole of ions corresponds to the gram atomic weight of the substance. Thus a mole of hydrogen ion is 1 gram and a mole of hydroxyl ion 17 grams per liter of solution, the atomic weight of hydrogen being 1, and the combined atomic weights of hydrogen and oxygen being 17. A liter of pure water therefore contains one ten-millionth of a gram of hydrogen ion and 17 ten-millionths of a gram of hydroxyl ion. The rest of the water molecules remain undissociated. A briefer way of expressing 1/10,000,000 is to write it 1×10^{-7}, or simply 10^{-7}, the negative exponent indicating that the number belongs in the denominator of a fraction. The dissociation constant of pure water has been shown to be 1×10^{-14}. Thus no matter what the respective concentration of the hydrogen ion or of the hydroxyl ion, the sum of their concentration is constant. From this it follows that when the concentration of hydrogen ion increases, from whatever source it may be derived, there is a corresponding decrease in the hydroxyl ion, and vice versa.

Since in pure water both the hydrogen ion and the hydroxyl ion are present in equal amounts, pure water does not exhibit either acidic or basic properties, i.e., it is perfectly neutral. If just enough acid is added to pure water to increase its hydrogen ion concentration tenfold, then one

liter of solution will contain 1/1,000,000 mole, or 10^{-6} mole, while in the same solution the hydroxyl ion concentration will have been reduced to 1/100,000,000 mole, or 10^{-8}.

This is a rather cumbersome way of expressing hydrogen ion or hydroxyl ion concentrations, made doubly awkward when decimal fractions must be used. To overcome this shortcoming, S. P. L. Sorensen devised the pH scale. The term pH is an expression meaning the logarithm to the base of 10 of the reciprocal of the hydrogen ion concentration. Stated more simply and non-mathematically, the pH value of a solution represents that figure which would normally be the negative exponent, with the negative sign omitted. Thus it has been stated that the hydrogen ion concentration of pure water is 10^{-7} mole per liter, which in terms of pH values is expressed as pH 7. A solution containing 10^{-6} mole of hydrogen ion per liter is given a pH value of 6. Since the scale is logarithmic, a difference of one whole unit means an actual tenfold difference in quantitative concentration of hydrogen ion. Thus a solution having a pH value of 6 contains ten times the concentration of hydrogen ion present in a solution having a pH value of 7. Since the hydroxyl ion concentration is the reciprocal of the hydrogen ion concentration, the sum of their exponents being equal to -14, the value for hydroxyl ion concentration is known from the figure of the hydrogen ion concentration and only the latter value need be used. The range of the pH scale lies between 0 and 14, with the midpoint 7 representing true neutrality. pH values below that figure indicate increasing hydrogen ion concentration or increasing acid reaction. At pH values above 7, the hydroxyl ions predominate and the reaction is alkaline. One need only remember, therefore, that acidity increases with decreasing pH values below the midpoint of 7, and that alkalinity increases as the number increases above 7. The relationships between pH values on the one hand, and grams of hydrogen ion per liter of solution and the corresponding degree of acidity or alkalinity on the other, as well as the pH values of familiar substances are summarized in Table 29 by J. L. St. John (*119*).

In Table 30 are given the approximate pH values of various acids and bases. The values shown all refer to $\frac{1}{10}$ normal solutions, i.e., solutions of equal concentration. The rather wide range in pH values exhibited by the acids and bases shows the great variation in ionic dissociation that characterizes these various acids and alkalis and determines their strength.

Buffers. Buffers may be defined as substances which, by their presence in solution, increase the amount of acid or alkali that must be added to bring about a unit change in pH. They thus act to prevent sudden or drastic changes in the hydrogen ion concentration when strong acids or

TABLE 29. pH COMPARISONS AND VALUES FOR FAMILIAR SUBSTANCES

Grams of H ions per liter of solution	No. of times acidity or alkalinity exceeds that of pure water (pH 7.0)	pH	pH of familiar substances
	10,000,000 ↑	↑ 0	
1/10	1,000,000	1.0	—0.1 *N* Hydrochloric acid
1/100	100,000	2.0	—Human gastric contents
			Vinegar
			0.1 *N* Acetic acid
1/1,000	10,000	3.0	—Apple juice
1/10,000	1,000	4.0	—Methyl orange changes
			color
	acidity	Increasing acidity	Grapes
1/100,000	100	5.0	—Molasses
			0.1 *N* Boric acid
			Bread
1/1,000,000	10 ↓	6.0	—Milk
			Flour
1/10,000,000	1 (pure water)	Neutral 7.0	—Pure water
			Saliva
1/100,000,000	10 ↑	8.0	—Baking soda
1/1,000,000,000	100	9.0	—Phenolphthalein changes
		Increasing alkalinity	color
1/10,000,000,000	1,000	10.0	—Soap
1/100,000,000,000	10,000	11.0	—Washing soda
	alkalinity		Trisodium phosphate
1/1,000,000,000,000	100,000	12.0	—Lime water
1/10,000,000,000,000	1,000,000	13.0	—0.1 *N* Sodium hydroxide
	10,000,000 ↓	↓ 14.0	

bases are added to a system. They perform an exceedingly important function in biological solutions or systems, such as fermenting dough, by stabilizing a suitable reaction level in the medium and thereby permitting yeast and the enzymes to function within favorable pH ranges which would otherwise be rapidly modified by reactive by-products.

TABLE 30. APPROXIMATE pH VALUES OF VARIOUS ACIDS AND BASES

Acids	pH Value	Bases	pH Value
Hydrochloric acid	1.0	Sodium bicarbonate	8.4
Sulfuric acid	1.2	Borax	9.2
Phosphoric acid	1.5	Ammonia	11.1
Sulfurous acid	1.5	Sodium carbonate	11.6
Acetic acid	2.9	Trisodium phosphate	12.0
Alum	3.2	Sodium metasilicate	12.2
Carbonic acid	3.8	Lime (saturated)	12.3
Boric acid	5.2	Sodium hydroxide	13.0

Buffers are generally weak acids or bases, that is, acids or bases which dissociate only slightly, and their corresponding salts. They include acetic acid and acetates, citric acid and citrates, carbonic acid and carbonates, phosphates, proteins, and others. The theory of buffer action may be exemplified by a consideration of the behavior of acetic acid and sodium acetate.

It has been shown above that acetic acid dissociates only very slightly into hydrogen ions and acetate ions.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

The degree or extent of dissociation is governed by a fixed ratio of undissociated acetic acid molecules to the free hydrogen and acetate ions. This ratio is known as the dissociation constant and represents an equilibrium which is characteristic for a given acid or alkali. If we were now to add sodium acetate to this solution, this equilibrium would be upset because the salt is almost completely dissociated and would hence supply an excess of acetate ions. There is thus a tendency for the excess acetate ions to unite with the free hydrogen ions to form undissociated acetic acid molecules and the quantity of the latter will increase until the characteristic equilibrium is reestablished.

Given such an acetic acid-sodium acetate solution, it is rather easy to visualize the reaction which occurs when a strong acid, such as hydrochloric acid, is added. Since hydrochloric acid dissociates completely into hydrogen ions and chloride ions, the new supply of hydrogen ions will unbalance the existing equilibrium. The acetate ions hence unite with the hydrogen ions from the hydrochloric acid and remove them from the solution in the form of undissociated acetic acid molecules. Hence the hydrogen ion concentration is not perceptibly increased as long as acetate ions are available to react with the hydrogen ions supplied by the added acid. However, once the supply of acetate ions is exhausted, no further reaction can occur and the pH of the solution will decrease, i.e., its hydrogen ion concentration will increase. Thus buffers are effective only within certain limits and generally their action is restricted to certain parts of the pH scale.

The addition of a base, such as sodium hydroxide, to the acetic acid-sodium acetate solution works analogously. Here, however, the hydroxyl ions supplied by the base react with the hydrogen ions of the acetic acid to form undissociated water molecules and thereby keep the concentration of the hydroxyl ions at a low level. The acetic acid will dissociate as long as a need for hydrogen ion exists and the ultimate result is a reduced concentration of undissociated acetic acid in the solution without a perceptible change in the pH.

pH Determinations. The two general methods for the determination of the pH value of solutions are the colorimetric and the electrometric. The colorimetric method is based upon the fact that certain common indicators change colors at certain pH levels which are characteristic for each individual indicator. Thus phenolphthalein is colorless in acid solution, but turns pink at pH 8.2, and the color deepens with increasing alkalinity to a clear red at about pH 10. Methyl orange, again, is red in solutions having a pH value below 3.1 and turns to yellow-orange when the pH is increased to 4.4, the zone between these two values showing gradual changes from red to orange. Indicators for all ranges in the pH scale are available. By stabilizing indicator solutions at different pH values through the addition of suitable buffers, it is possible to prepare stable color standards which will cover the entire usable range of pH values. To determine the pH of the unknown solution a measured amount of the proper indicator is added and the color developed compared with the buffered color standards. Sets of color standards for use with comparator blocks are available in sealed comparison tubes through commercial laboratory supply houses and hence the chemist is relieved of the task of preparing these standards himself. Colorimetric determinations yield fairly accurate results with colorless or only slightly colored solutions but are difficult to execute with highly turbid solutions.

Electrometric methods of various types are employed when greater precision is desired or when the colorimetric method cannot be applied. Modern electrometric pH instruments have been simplified to a point where they can be used for routine determinations by individuals possessing only limited training in chemistry. A number of compact industrial instruments using the glass electrode are available which give readings of sufficient accuracy for most ordinary purposes. The theory underlying the electrometric determination is discussed in detail in several texts which should be consulted by those wishing more specialized information on this subject (*120, 121, 122*).

pH in Baking. pH plays a highly significant role in the production of both yeast raised and chemically leavened products. In bread production it exerts its principal effect during fermentation where it controls yeast activity, amylolytic action, gluten behavior and the survival of rope-producing organisms. The decisive pH level is at a value of 5 which approximates the isoelectric point of gluten and represents the near optimum for the rate of fermentation and diastatic activity. Also, doughs slightly more acid than pH 5 are largely protected against rope infection. In the case of chemically leavened baked products, pH is of great importance in determining the color and texture of the finished goods. Thus in devils food cakes, the color of the cake may range from a light brown at a pH

of 7.0 to 7.5, to a dark mahogany red color at a pH of 8.8 or 9.0. At the same time, the texture tends to become much finer as the pH level increases. Excessively high pH must be guarded against, however, since it may cause an objectionable alkaline flavor. In the case of white layer cakes, the color tends to change from white to a dull yellow as the pH increases beyond 7, and the product becomes more crumbly (*123*). Finally, each product has its optimum pH value for best keeping quality.
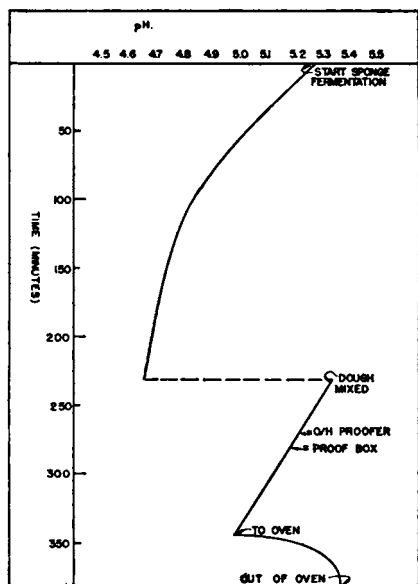
FIG. 32—pH profile of baking process using a lean commercial sponge-dough procedure. (*Courtesy J. C. Patterson Co.*)

The curve in Fig. 32 charts the course of pH in bread production (*123*). This particular study was made on a lean formula processed by the sponge-dough method. It will be noted that during the sponge fermentation, the pH decreases from an initial value of approximately 5.3 to 4.7, the decrease being rather more rapid during the first two hours of fermentation than the second two hours. The addition of the remainder of the dough ingredients largely neutralizes the acidity formed during sponge fermentation and the pH is raised to approximately its initial value of 5.3. On subsequent dough fermentation during floor time, the intermediate proof and the final proof, acidity again increases, depressing the pH to a level of about 5.0. On baking for thirty minutes, the pH increases to 5.4. These changes in pH value during the course of baking are readily explainable on the basis of the effect of yeast fermentation and heat. The acids formed by yeast during fermentation, consisting principally of lactic acid and acetic acid, may logically be expected to lower the pH of the dough since they show some degree of ionization. Upon remix of the sponge, the addition of fresh ingredients largely nullifies the acidifying effect of sponge fermentation by the introduction of neutralizing ingredients. Finally during baking the pH is again increased by the volatilization and removal of a great proportion of the organic acids. Thus, in general, a bread with a pH value lower than 5.4 may result either from too long a fermentation or too short a baking time, while bread with a pH value higher than 5.7 is a characteristic product of a young dough (*123*).

Harrel, Brown and Johnson (*124*) have also recently discussed the significance of pH in baking and milling. pH control in milling is of practical significance principally in connection with the chlorine treatment of cake and cookie flours. Chlorine is used rather extensively as a flour improver and bleaching agent for soft wheat flours. Because chlorine treatment results in the formation, or rather dissociation, of hydrogen ions, the pH value of the treated flour is lowered in correspondence with the severity of treatment so that pH determination constitutes an important control test on chlorine-bleached flour. It has been shown that the improving action obtained with chlorine is independent of the decline in pH since subsequent treatment with ammonia will again raise the

Fig. 33—Effect of cake flour maturation on volume. Cake layers at right made from untreated flour. (*Courtesy Pillsbury Mills.*)

pH without, however, materially changing the beneficial maturing results. The maturing action of chlorine is very necessary and important in the production of cake and cookie flours.

The pH value of flours obtained from wheat mixtures is largely a function of flour grade. In general the more highly refined patent flours are more acid and hence have a somewhat lower pH value than do the lower grades of flour.

It has previously been pointed out that enzymes are characterized by certain optimum pH levels at which their maximum activity under given conditions is exerted. This holds true also of the enzymes encountered in baking. Thus the optimum pH level for diastase is 4.4 to 5.2, maltase, 6.7 to 7.3, papain, 4.0 to 7.0, and lipase, 4.7 to 5.0. In general, when the pH is changed from the optimum by one whole unit in either direction, the activity of amylase is reduced by one half. Amylases, in common with other enzymes, show different optimum levels at different temperatures. Thus Harrel *et al.* (*124*), found the relationship between temperature and pH for optimum amylase action to be as shown in Table 31.

Stamberg and Bailey (*125*) determined the pH values of several white, yellow, chocolate and angel food cakes obtained from various commercial bakeries. The values are shown in Table 32.

TABLE 31. RELATIONSHIP OF TEMPERATURE AND PH
FOR OPTIMUM DIASTATIC ACTION

Temp. ° F.	Temp. ° C.	pH optimum
77.0	25	4.4
113.0	45	5.0
140.0	60	5.7
156.2	69	6.1

It will be seen that the average pH for white cakes was 7.47, yellow cakes 7.59, chocolate cakes 8.48, and angel food cakes 5.67. The same authors had determined the optimum pH range of white and yellow layer cakes, with respect to flavor and eating quality, to be 7.0-7.9, so that with but one exception all of the white and yellow layer cakes were within the

TABLE 32. THE pH OF SOME COMMERCIAL CAKES FROM VARIOUS TYPES
OF BAKERIES

Type of bakery	White cakes	Yellow cakes	Chocolate cakes	Angel food cakes
Chain retail	7.08	—	7.96	5.33
" "	7.29	—	7.93	—
" "	7.68	—	8.63	—
Retail	7.22	7.68	8.89	6.48
"	7.95	7.69	8.81	—
"	—	—	8.47	—
Wholesale	7.61	7.39	8.49	5.44
"	—	—	8.71	5.43
Average pH	7.47	7.59	8.48	5.67

optimum range. In general, white and yellow cakes with a pH value outside the range of 7.0-7.9 are of an inferior quality, while the most suitable range appears to be 7.22 to 7.35.

Table 33, taken from data by Harrel (*126*), gives the proximate pH ranges and values of baked products and raw materials employed by the baker.

OXIDATION AND REDUCTION

The earliest and most common concept of oxidation involved a reaction in which oxygen was chemically added to or combined with a substance. Thus an ordinary metal exposed to atmospheric oxygen will corrode, forming an oxide which is a compound consisting of the metal and oxygen. The metal is said to have become oxidized. A great many substances, both organic and inorganic, are oxidizable in this sense. The term reduction was applied to the reverse process, namely the removal of oxygen from a compound. Thus when heated iron oxide is exposed to a stream

of hydrogen gas, the oxygen of the oxide combines with the hydrogen to form water, while the iron is set free. Hence the earliest definition of oxidation and reduction referred only to the addition and removal, respectively, of oxygen during chemical reactions.

TABLE 33.   pH VALUES FOR BAKED PRODUCTS AND RAW MATERIALS

Material	pH
Angel food cake	5.0-6.5
Bread, rye	4.3-4.7
Bread, white	5.0-6.0
Cherries	3.8-4.0
Chocolate, dutched	6.0-7.8
Chocolate, natural	5.1-6.2
Chocolate cake	7.2-7.6
Cocoa, dutched	6.0-7.5
Cocoa, natural	5.2-6.0
Cookies	6.5-8.0
Crackers	7.0-8.5
Devils food cake	7.5-8.4
Doughnuts	6.5-8.0
Doughnut flour	6.0-7.0
Egg yolk	5.9-6.8
Egg white	7.6-9.7
Flour, unbleached bread	5.8-6.0
Flour, white bleached	5.7-5.9
Flour, rye	6.6
Fruit cake	4.4-5.0
Jam	3.5-4.0
Jelly	3.0-3.5
Lemons	2.2-2.4
Limes	1.8-2.0
Milk	6.3-6.8
Molasses	5.0-5.4
Pound cake	6.6-7.1
Sponge cake	7.3-7.6
Vinegar	2.4-3.4
Water, dist., CO_2 free	6.8-7.0
White layer cake	7.1-7.4
Yeast	3.7-7.1
Yellow layer cake	6.7-7.1

Later it was realized that reactions occurred which did not involve the transfer of oxygen but which nevertheless fell into the general category of oxidation-reduction reactions. Thus, when oxygen is bubbled through a solution of methylene white, or leuco methylene blue, the colorless compound is changed to methylene blue which is a blue dye, some oxygen being used up in this reaction. However, careful analysis has

shown that methylene blue does not contain oxygen and differs from leuco methylene blue only by having two hydrogen atoms less. Hence leuco methylene blue has been oxidized by the withdrawal of two hydrogen atoms which combined with oxygen to form water. The methylene blue may again be reduced and rendered colorless by the addition of two hydrogen atoms. In view of this, the original concept of oxidation and reduction had to be expanded to include the withdrawal and addition, respectively, of hydrogen.

With the development of the modern atomic theory which stipulates the presence of electrons of unit negative charge within atoms, the theory of oxidation and reduction received its final formulation. Thus it was observed that when oxygen is introduced into a solution of cuprous chloride (CuCl), this salt is changed into cupric chloride ($CuCl_2$), according to the following equation:

$$4CuCl + 4H_2O + O_2 \rightarrow 2CuCl_2 + 2Cu(OH)_2 + 2H_2O$$

Since the cuprous ion possesses only one positive charge produced by the loss of one electron, and the chloride ion (and OH ion) possesses one negative charge obtained through the gain of an electron, the cuprous ion has to give up one additional electron to assume the bivalent positive charge necessary to bind two negatively charged chloride ions. Hence oxidation in this case involves the transfer of electrons. The same process occurs also in the complete absence of oxygen, as when cuprous chloride and ferric chloride are reacted to yield cupric chloride and ferrous chloride. The equation for this reaction is as follows:

$$CuCl + FeCl_3 \rightarrow CuCl_2 + FeCl_2$$
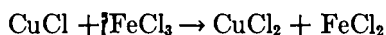
To show the changes in electric charge involved, the same equation may be expressed ionically and becomes:

$$Cu^+ + Fe^{+++} \rightarrow Cu^{++} + Fe^{++}$$
$$\text{-ous} \quad \text{-ic} \quad \quad \text{-ic} \quad \text{-ous}$$
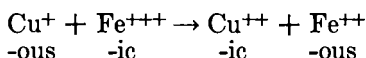
Numerous such reactions are encountered in which the substance being oxidized loses electrons while the substance being reduced gains electrons. From this observation the popular modern definition of oxidation and reduction is derived: Oxidation is a change involving the loss of electrons; reduction involves the gain of electrons, regardless of whether gains or losses of oxygen and hydrogen are involved. Since an electron set free by an oxidation cannot exist independently but must be taken up by some other substance, it is clear that an oxidation must always be accompanied by a reduction.

Since an oxidation-reduction reaction involves a transfer or flow of electrons, the assumption lies close at hand that electrical potentials are set up in oxidation-reduction systems which can be measured. Thus, if an electrode of gold or platinum is immersed in an oxidation-reduction system, such as Fe^{++}/Fe^{+++}, in the presence of acid, and if the system contains both the oxidized form (oxidant) and the reduced form (reductant), a potential is set up at the electrode, which can be measured by the usual potentiometric method against a standard normal hydrogen electrode. The magnitude of this potential depends upon the ratio of concentrations of the oxidized and reduced forms present, and its value (E_h) in volts can be expressed by the equation:

$$E_h = E_o + \frac{RT}{nF} \log_e \frac{[\text{oxidized state}]}{[\text{reduced state}]}$$

where E_o is a constant, known as the standard oxidation-reduction potential of the system, R is the gas constant, T the absolute temperature, F the faraday (96500 coulombs), and the square brackets represent concentrations or, more strictly, activities, of the respective states. By introducing the known values of R and F, and converting natural logarithms to those having a base of 10, the equation becomes

$$E_h = E_o + \frac{0.0002T}{n} \log \frac{[\text{oxidized state}]}{[\text{reduced state}]}$$

The actual potential of a given system thus depends on the relative concentrations of the two states; when these are equal, the ratio is unity and the logarithm zero, then E_h is equal to E_o.

It is not necessary here to discuss in detail the mathematical and thermodynamic reasoning upon which the derivation of the E_h is based. It should be understood, however, that E_h measures only the tendency to oxidize or reduce and not the total amount of oxidation or reduction possible, since this potential is determined by the relative and not the absolute concentrations of oxidant and reductant in a system. Also, since most oxidation-reduction systems involve substances capable of ionization, and since the degree of ionization is altered by changing pH values, it is readily apparent that the oxidation-reduction potential, or redox potential, is liable to be changed with changes in pH.

It has been indicated above that the redox potential uses as a standard of reference the normal hydrogen electrode which is an electrode of platinum in hydrogen gas at one atmosphere pressure and in contact with a solution approximating pH 0. This relation of the redox potential to hydrogen pressure has made possible the derivation of an equation which expresses the redox-potential in terms of rH which represents the loga-

rithm of the reciprocal of the pressure of reducing hydrogen just as, analogously, the term pH is the logarithm of the reciprocal of the hydrogen ion concentration of a solution. The use of the concept rH is not without objection since it implies the presence in the reducing systems under consideration of hydrogen as a universal reductant. This implication is by no means generally justifiable.

Analogous to the pH scale, there has been devised an rH scale ranging in values from 0 to 42 on which the individual rH values represent the negative logarithm of an assumed hydrogen pressure of a solution. This hydrogen pressure is indicative of the magnitude of the reducing capacity of an aqueous solution. The value 0 on the rH scale corresponds to a hydrogen pressure of 1 atmosphere. As the value increases on the rH scale, the hydrogen pressure decreases and there is a corresponding decline in reducing capacity. At the same time, however, the oxidation capacity increases at an identical rate until a value of 42 has been reached which corresponds to a hydrogen pressure of 10^{-42} or the practical absence of hydrogen. From the above considerations it is evident that, for example, an rH value of 5 signifies the reducing power of hydrogen exerting a pressure of 10^{-5}, or 1/100,000, atmospheres, just as, analogously, pH 5 represents the hydrogen ion concentration of 10^{-5} gram hydrogen ions per liter solution. An rH value of 15 indicates a reducing capacity corresponding to an assumed hydrogen pressure of 10^{-15}, or 1/1,000,000,000,000,000, atmospheres. Thus the higher the rH value of a solution, the lower is its reducing power on the one hand, and the greater is its oxidizing power on the other. This may also be expressed as follows: With an increasing oxidizing power of a solution the rH changes in a positive direction, whereas with an increasing reducing power the rH shifts in a negative direction. Within the scale, a medium with an rH value higher than 25 is definitely oxidizing in character, while one with an rH value below 15 is characterized as reducing. The range within rH value 15 to 25 is designated as being neither strongly oxidizing nor reducing in character.

The redox potential or rH value can be determined by one of two methods. One is the usual potentiometric method which, because the determination must be carried out in the complete absence of oxygen, presents certain difficulties. A more convenient colorimetric method is also available which makes use of certain redox indicators which change in color, or decolorize completely, at specific rH values, similar to the change in color observed with pH indicators. Table 34 by Rippel (*127*) gives a list of oxidation-reduction indicators covering the rH range of 2 to 29.

The rH value of a system, such as dough, is determined by a variety of substances possessing oxidizing or reducing properties, the prevalence of

one type over the other determining the over-all rH value of the entire system. In a dough made with green flour the presence of certain potent reducing agents imparts a reducing character to the mass. Experience has shown that for every flour there exists a definite optimum oxidation potential for the best baking characteristics. Since this optimum potential is seldom encountered naturally with flour, except after long storage during which atmospheric oxygen exerts its oxidizing effect, the practice of using oxidizing agents either at the mill or in the bakery to improve the baking quality of flours has become general.

TABLE 34. OXIDATION-REDUCTION INDICATORS

	Transition	rH range
Neutral red	red to colorless	2 - 4.5
Safranine T	red to colorless	4 - 7.5
Indigo disulfonate	blue to yellow	8.5-10.5
Indigo trisulfonate	blue to yellow	9.5-12
Indigo tetrasulfonate	blue to yellow	11.5-13.5
Methylene blue	blue to colorless	13.5-15.5
Thionine	violet to colorless	15 -17
Toluylene blue	violet to colorless	16 -18
Thymol indophenol	blue to colorless	17.5-20
m-Cresol indophenol	blue to colorless	19 -21.5
2,6-Dichlorophenol indophenol	blue to colorless	20 -22.5
Diphenylamine sulfonic acid	violet to colorless	27 -29

The recognition of the importance of oxidation-reduction reactions to baking quality has resulted in extensive studies on this subject. While much work remains to be done, considerable progress has been made, only the highlights of which will be touched upon here.

When a freshly milled, otherwise untreated flour is processed into bread, unsatisfactory results are obtained. In the absence of yeast food, such flours yield doughs which are usually characterized as "green" or "underdeveloped"; they are too soft and flexible, lack elasticity, and fail to give adequate oven spring. Bread made from such doughs has small volume, an open cell structure, coarse harsh texture, poor crumb color, and a smooth crust without signs of a break. The extent to which these "green" characteristics appear in an unstored, unbleached flour differs greatly with different flours. Flours exhibiting such "green" or reduced properties are seldom encountered in commercial practice since mills normally subject all their bread flours to artificial bleaching and oxidation. Unbleached flours, when properly aged by prolonged storage, also lose their "green" character. It is only accidentally that reduced flours reach the commercial baker. Hites (128) mentions the possibility that when wheats are exposed for excessive periods of time to such fumigants

as carbon disulfide or hydrogen cyanide, the flour components of wheat may be reduced to a point where normal amounts of bleaching agent and yeast food will fail to produce adequate oxidation.

When doughs from moderately matured flours are treated with small increments of yeast foods containing oxidizing agents, such as potassium bromate or potassium iodate, they become more elastic, tighter, less sticky and exhibit more life than do untreated doughs. Such doughs usually also give a superior oven spring. The resultant bread has a good volume, its crust shows a smooth break, and its cell structure is even with small, thin-walled cells, and its texture is soft and velvety. The marked difference in bread character obtained from immature or green flour and from properly aged or oxidized flour is shown in the following figure.
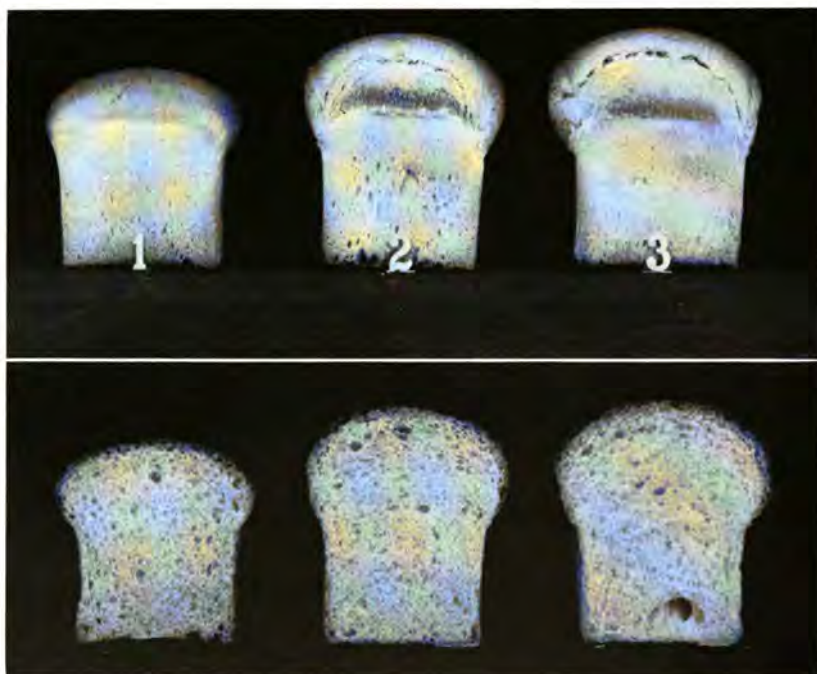
Fig. 34—Comparison of loaves whose doughs received normal amounts of potassium bromate. No. 1—check loaf; No. 2—2 mg % $KBrO_3$; No. 3—3 mg % $KBrO_3$.

When too much oxidizing agent in the form of yeast food is added to a dough, over-oxidation results. Over-oxidized doughs become excessively bucky, resist distortion during molding and tear easily. The doughs may break open during proofing because of resistance of the gluten to expansion. Bread made from such doughs has a small volume with rough,

uneven crust which usually shows large unsightly breaks. Its crumb exhibits many ruptured cells and may have large holes.

The effect of excessive potassium bromate additions to dough has been investigated by Freilich and Frey (*129*). They designated the effect as the "excess bromate" effect and described the resultant bread as being characterized by "a loaf of poor volume, rounded corners, rough exterior, a tendency to form a peak on the upper part of the loaf, and poor, heavy,
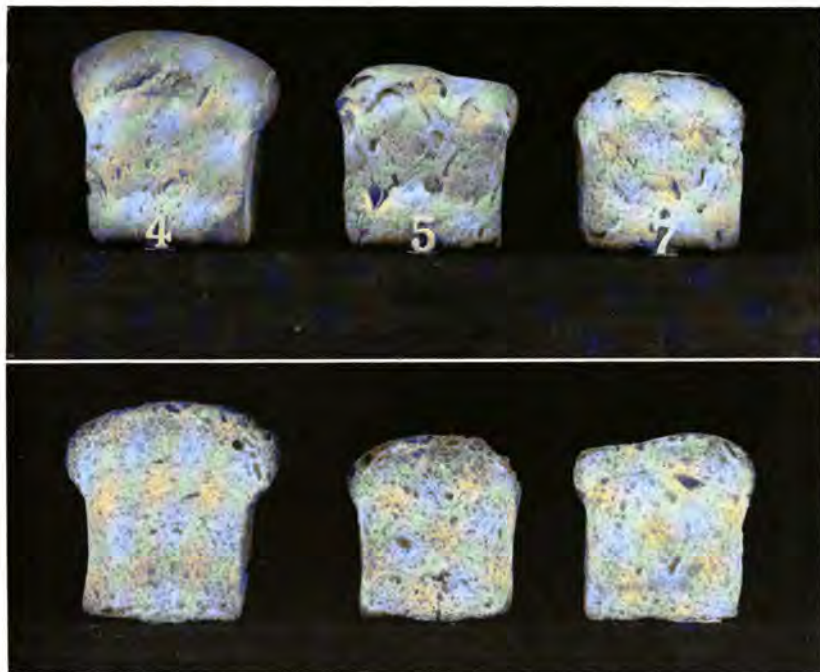
FIG. 35—Comparison of loaves whose doughs received abnormal quantities of potassium bromate. No. 4—2 mg % $KBrO_3$; No. 5—4 mg % $KBrO_3$; No. 7—6 mg % $KBrO_3$.

lumpy, coarse texture." This effect is particularly apt to be produced in lean, straight dough formulas. The over-treated dough is bucky in character, this buckiness being apparently different from that obtained by direct inhibition of proteolytic enzymes. The same authors (*130*) found that if an over-bromated dough is remixed after fermentation the "excess bromate" effects are completely neutralized. Remixing, however, must be carefully controlled since excessive remixing results in bread of decreased loaf volume and bread quality.

The important role which oxidation plays in bread quality was underlined by these authors who studied the effects of mixing in oxygen and

other gases, and of additions to the dough of oxidizing and reducing agents. Jorgensen, in his proteolytic enzyme theory, has attributed the beneficial effects of oxidizing agents to their inhibiting action on proteolytic enzymes which otherwise would tend to degrade the gluten structure excessively. Conversely, the harmful effects of reducing agents, such as glutathione and cysteine, were ascribed to the activation of proteases by these substances. Freilich and Frey found that the effects obtained by bromate were far more profound than mere proteinase inhibition. They obtained effects similar to the bromate effects by mixing dough in oxygen and expressed the belief that the beneficial result is to be attributed to the action of oxygen on some flour constituents other than the enzyme (*131*). When protease or glutathione is added to a dough which otherwise would yield a normal loaf of bread the resultant bread has a low volume and poor quality. The harmful effects of protease and glutathione may be overcome by the addition of proper amounts of an oxidizing agent, such as potassium bromate, so that normal bread is again produced. The same improving effect is also obtained by mixing the dough in oxygen gas. If too much bromate is added, however, the result is a poor loaf showing "excess bromate" characteristics. This in turn can be corrected by remixing the dough after fermentation for a proper period of time. If the remixing is too prolonged, the dough breaks down and results in poor bread. By replacing air with another gas, such as nitrogen, the effects of excessive remixing may also be overcome and normal bread again obtained. These various functions of the different agents and factors are summarized in the following diagram reproduced from the paper of Freilich and Frey.
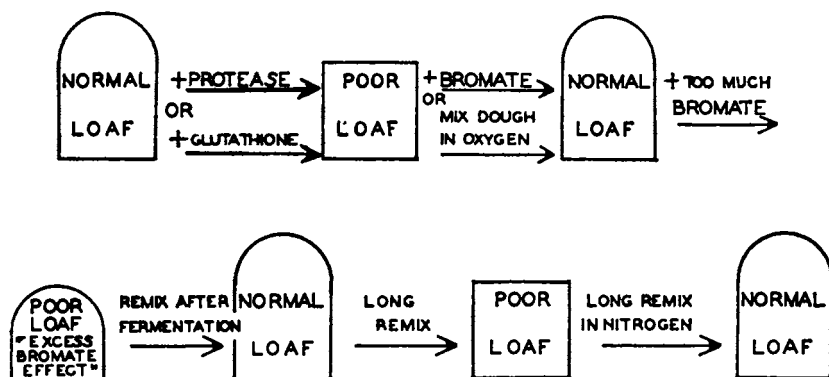
Fig. 36—Diagrammatic representation of interrelationships of oxidation and mixing in bread doughs. (*Courtesy Cereal Chemistry.*)

The green or reduced characteristics of freshly milled flour and immature doughs appear to be associated with the presence in the flour

protein of sulfhydryl (SH) groups. Thus when substances containing the SH group, such as glutathione and cysteine, are added to dough, the result is a slackening and eventual liquefaction of the dough. It is thought that reducing agents either attack the disulfide (S-S) linkages of proteins, changing them to SH linkages, or if they contain SH groups themselves, attach themselves to the flour protein. Oxidizing agents, on the other hand, appear to attack SH groups and change them into S-S linkages or they convert the SH groups into oxygen compounds. The action of reducing agents is as a rule readily reversible, whereas oxidation is more difficult to reverse. The availability of a positive test for the presence of SH groups in flour has made possible the study of the chemical effects of oxidizing agents. Thus Baker, Parker and Mize (*132*) showed that treatment of flour with nitrogen trichloride at the rate of 6 g. of the bleach per barrel of flour removed about 22 percent of the sulfhydryl groups, and that chlorine treatment at the rate of 2 oz. per barrel removed about 20 percent. Storage of flour at room temperature for six months caused a sulfhydryl loss of 16 percent, while storage in a refrigerator for the same period did not reduce the sulfhydryl content of flour. While thus only relatively small proportions of the total SH groups are oxidized by bleaching agents or natural aging, these appear to constitute the most reactive groups.

It is known that the requisites for elasticity in polymers are, first, a long chain, and second, cross-linkages joining the linear polymers at intervals to form a three-dimensional network. The gluten proteins in dough provide the linear polymer, but little experimental evidence exists as to the identity of the cross-linkages, although the disulfide linkages are assumed to be involved (*133*).

Hlynka (*134*) has recently produced additional proof that disulfide linkages are in all probability involved in the gluten structure. By treating gluten with small amounts of sodium bisulfite, which had previously been shown to dissociate disulfide linkages in wool, he found that the gluten became soft, sticky, and inelastic; larger amounts of bisulfite destroyed the gluten-yielding property of a dough entirely. This effect of bisulfite may, however, be prevented or reversed by the addition of acetaldehyde which binds the bisulfite and removes it from the reacting system. Thus if a reagent is added which specifically destroys and splits disulfide linkages, the gluten structure disintegrates, while if this reagent is removed from the system, gluten structure reforms and regains its elasticity. The same author also suggests that the carbonyl groups of reducing carbohydrates may act as cross-linking agents between protein chains.

Oxidation reactions in dough are not entirely confined to the SH groups

of proteins, but involve other reducing substances as well. While the actual mechanism of the oxidation and reduction reactions in flour and dough is still only partly understood, its practical importance has served as an incentive to research which has elucidated some of the basic facets of the problem. Sullivan (*135*) has prepared a highly readable summary of the present status of our knowledge of this subject.

PART II—MATERIALS OF BAKING

CHAPTER VIII

WHEAT FLOUR

CLASSES AND VARIETIES OF WHEAT

Wheat represents the second largest field crop in the United States, being exceeded only by corn or maize. From the viewpoint of human nutrition, however, this cereal supersedes all others in importance. Thus, in the United States, food products made from wheat contribute approximately one-fourth of the total food energy requirements of man, and in some European countries, notably France and Italy, wheat's share in human nutrition is nearly twice as great. The reasons for this preeminence of wheat as a food cereal are many. It is well adapted to the soil and climatic conditions that prevail in large areas of the world. The wheat plant is high yielding and rather easy to cultivate. The mature grain has excellent storage properties and a high food value. Its yield of suitable flour upon processing is relatively high and there is practically no waste since the by-products of milling are used for animal feed. The unique characteristics of the wheat proteins, which upon wetting and mixing give rise to gluten, permit the production of a yeast-leavened light bread which has served mankind as of the principal food items since the dawn of history.

Wheat grown in the United States belongs to three distinct botanical species. By far the most important of these is *Tricitum vulgare,* or common wheat, which comprises nearly 95 percent of the total production (*136*). The two other less important species are *Tricitum durum,* which comprises the amber and durum wheats, and *Tricitum compactum,* which includes the red and white club wheats.

Nearly 200 distinct varieties of common wheat were grown in the United States in 1944 (*137*). Differences among these varieties include such factors as presence or absence of awns, possession of varying degrees of color pigments, hardness or softness of kernel texture, resistance to cold, drought and plant diseases, strength of straw, period of ripening, and milling and baking characteristics. The common wheats are grouped into four major categories: hard red spring, hard red winter, soft red winter, and winter and spring white wheats. Winter wheats are planted in the fall in regions where the winters are only moderately severe and relatively dry. They begin to grow prior to the onset of cold weather,

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become dormant during winter, and resume their vigorous growth in the spring. They attain maturity in early summer. The spring wheats comprise varieties grown in regions where winters are too severe for winter varieties. They are sown in the spring and harvested in late summer.

The total seeded acreage of wheat in the United States in 1944 was slightly more than 65½ million, which is approximately 1¾ million acres larger than in 1939 (*137*). Hard red spring wheat was grown in 23 states in 1944, and was the leading class in Minnesota, North Dakota, South Dakota, and Montana. Hard red winter wheat was grown in 30 states, with greatest acreage occurring in Kansas, Nebraska, Oklahoma, Texas, and Colorado. Soft red winter wheat was produced in a total of 33 states and is the leading class in the eastern states, with largest acreages in Ohio, Missouri, Indiana, Illinois, and Pennsylvania. White wheat is grown chiefly in the far western states, and in New York and Michigan. Durum wheat was grown in 10 states, the principal producing states being North Dakota, South Dakota, and Minnesota.

The estimated acreage and percentage of the total wheat area of the United States occupied by each of the five classes of wheat are given in the following table (*137*).

TABLE 35.   DISTRIBUTION OF PRINCIPAL WHEAT CLASSES

Class	Total wheat area occupied						1939	1944
	1919	1924	1929	1934	1939	1944	Acres	Acres
	per-cent	per-cent	per-cent	per-cent	per-cent	per-cent		
Hard red spring..	24.2	22.4	22.0	23.2	20.9	24.0	13,330,648	15,765,582
Durum[1].........	6.4	8.2	9.4	4.6	5.3	3.3	3,372,405	2,179,258
Hard red winter..	32.0	41.4	43.5	44.6	47.6	46.8	30,456,919	30,709,456
Soft red winter...	30.1	22.1	17.7	20.9	19.6	18.2	12,552,634	11,937,179
White...........	7.3	5.9	7.4	6.7	6.6	7.7	4,198,394	5,092,525
Total........	100.0	100.0	100.0	100.0	100.0	100.0	63,911,000	65,684,000

[1] Includes durum and red durum classes.

The data in this table show that hard red winter wheats are allotted by far the greatest acreage, nearly twice that of the second most important class, the hard red spring wheats. The hard varieties are sown on approximately 70 percent of the total wheat acreage. Third in acreage come the soft red winter wheats, while the durum and white wheat varieties are grown on approximately 10 percent of the total wheat area.

According to the official grain standards of the United States (*138*) wheat is now separated into seven commercial classes, in five of which there are several subclasses. Each subclass, in turn, is divided into 5

grades and a sample grade. The commercial classes and subclasses are given in the following table.

TABLE 36. CLASSES AND SUBCLASSES OF WHEAT

Class I. Hard Red Spring Wheat
(a) Dark Northern Spring
(b) Northern Spring
(c) Red Spring

Class II. Durum Wheat
(a) Hard Durum
(b) Amber Durum
(c) Durum

Class III. Red Durum Wheat

Class IV. Hard Red Winter Wheat
(a) Dark Hard Winter
(b) Hard Winter
(c) Yellow Hard Winter

Class V. Soft Red Winter Wheat
(a) Red Winter
(b) Western Red

Class VI. White Wheat
(a) Hard White
(b) Soft White
(c) White Club
(d) Western White

Class VII. Mixed Wheat

The classification of subclasses into numerical grades ranging from 1 to 5 and a sample grade is based upon such factors as test weight per bushel, content of shrunken or broken kernels, presence of foreign matter such as stones or cinders, admixtures of other wheat varieties, freedom from objectionable foreign odors such as those of molds, smut, garlic, etc., and moisture content.

The hard wheat varieties, which include hard red spring, hard red winter, and hard white wheats, find their principal use in the production of flours for the making of high quality, yeast-leavened bread. The soft wheats, which include soft red winter, soft white, and white club wheats are particularly adapted to the production of chemically leavened baked products, such as cakes, pastries, cookies, etc. Amber durum wheats are suitable principally for the making of such alimentary pastes as noodles, macaroni, spaghetti, etc. Red durum wheat finds its main use as a poultry and livestock feed. The suitability of a wheat for any of these purposes is determined primarily by its protein content which, in turn, is associated to a marked degree with kernel texture. Thus the hard

wheats generally possess a high protein content, whereas soft wheats contain less protein in comparison.

Each wheat class contains a large number of individual varieties, the one differing from the other in one or more particular properties. Clark and Bayles (*139*) have provided a description, based on a varietal classification, of the wheats grown in the U. S. in 1939. The leading varieties in 1944 within each wheat class are given in Table 37 in the order of their relative importance.

TABLE 37.   RELATIVE RANKINGS OF WHEAT VARIETIES WITHIN THEIR CLASSES

Hard Red Spring	Durum and Red Durum	Hard Red Winter	Soft Red Winter	White Wheats
Thatcher	Durum[1]	Tenmarq	Thorne	Baart
Rival	Mindum	Turkey	Fultz	Federation
Ceres	Pentad	Blackhull	Clarkan	Dawson
Marquis	Kubanka	Chiefkan	Fulcaster	Yorkwin
Regent	Peliss	Early Blackhull	Kawvale	Rex
Pilot	Stewart	Cheyenne	Redhart	Goldcoin
Renown	Carleton	Kanred	Leap	Hymar
Vasta	Acme	Red Chief	Trumbull	White Federation 38
Reward	Kahla	Nebred	Nittany	Baart 38

[1] Varieties unknown to growers

The relative importance of individual varieties undergoes constant fluctuations with the passage of years. Thus, important varieties may reveal certain weaknesses which cause a decline in their popularity, while newly developed varieties may show great promise and assume a leading position. As an example, the variety Marquis was grown on 85 percent of all acreage devoted to hard red spring wheat in 1924. By 1944, its acreage had been reduced to slightly more than 9 percent. The reason for this decline was the variety's lack of resistance to stem rust.

Generally speaking, wheat classes may be distinguished by differences in such factors as protein content, water absorption, gluten quality, milling yield, etc. However, more frequently than not, greater differences may be found in wheats within a class than the general averages between classes. Shollenberger and Clark (*140*) compared a large number of samples of each class and obtained the average values given in Table 38.

On the basis of these data it would be difficult, if not impossible, to give a conclusive rating in the case of the two bread wheats of one class over the other. The hard red winter wheat, for example, is higher in test weight, flour yield, and water absorption, whereas the hard red spring wheat is higher in protein content, ash, and loaf volume, with the texture being the same for both wheats. Thus each wheat is superior to the other in some respects and their rating would depend upon the relative im-

portance assigned to the quality factors in which they excel. Soft wheats are definitely inferior to hard wheats for bread production but, on the other hand, they possess properties which render them far superior to the latter for the production of chemically leavened baked products. Durum wheats also are unsuitable for bread baking, but are unsurpassed for macaroni making purposes.

Environment exerts a profound effect upon the composition of wheat. It has been frequently observed that differences in composition brought

TABLE 38.   QUALITY MEASURES ON VARIETIES IN THE DIFFERENT WHEAT CLASSES

Class	No. of samples	Test weight cleaned wheat	Protein wheat	Yield straight flour	Ash in straight flour	Water absorption	Loaf Volume	Texture
		lbs.	%	%	%	%	cc.	%
Hard red spring..	1,128	58.5	13.9	69.6	0.49	59.9	2,210	89.5
Durum.........	387	60.3	15.5	71.1	0.77	62.4	1,943	89.5
Hard red winter.	334	61.1	13.5	72.4	0.45	61.1	2,028	89.5
Soft red winter..	189	60.5	11.3	71.0	0.46	56.1	1,929	87.7
White wheat....	511	60.1	12.3	70.6	0.47	57.2	1,876	86.9

about by environment may by far exceed differences due to variety. Thus Shollenberger and Clark (*140*) have reported a range of from 7.5 to 19.6 percent of protein in samples of Marquis wheat, the low-protein samples having been grown in California and the high-protein samples in Montana. Environment comprises climatic and soil conditions which are highly variable and may differ from year to year in the same locality, accounting thereby for the annual differences in the baking behavior of wheats belonging to the same variety and grown in the same region. It is generally known that climate determines the difference between spring and winter wheats and, to a large extent, between hard and soft wheats. Thus winter wheats are grown in regions, such as the Southwestern Plain states, where the winters are relatively mild, while spring wheats are restricted to areas where severe winters predominate. According to Swanson (*141*) local weather conditions, in respect to temperature and rainfall, as well as soil, are factors in the production of hardness and softness. The main characteristics which distinguish hard spring, hard winter, soft and white wheats are due mostly to climate. The influence of such factors as climate, irrigation, soil, and the use of fertilizers upon wheat composition has been reviewed in detail by Bailey (*142*).

Larmour (*143*) has subjected the published investigations into the comparative qualities of hard red winter and hard red spring wheats to a critical evaluation. Contrary to the widely held opinion that hard red

winter wheat varieties are inferior in general quality to the hard red spring wheats, Larmour concluded that the available experimental evidence justifies the placing of these two wheat classes on an equal par. He attributes the higher commercial rating which the hard red spring wheats have received to "(1) their higher average protein content, (2) their greater uniformity, and (3) their long established reputation for high quality." Fundamentally, both classes of wheat are equal in basic quality.

STRUCTURE OF THE WHEAT KERNEL

The wheat kernel, considered structurally, is differentiated into three distinct parts, namely the branny covering, the germ or embryo, and the endosperm. These structures and their position in the wheat kernel are indicated in Figure 37. From a biological viewpoint, the bran is the protective covering of the grain, the germ is the plantlet which on germination develops into a new plant, and the endosperm constitutes a relatively large reservoir of food for the growing seedling.

The wheat kernel has a rounded dorsal side and a creased ventral side. At its apex or stigmatic end the grain has a cluster of short fine brush hairs. The bran coat consists of several distinct layers. The outer bran layers constitute the pericarp or dry fruit coat and consist of the epidermis, epicarp, cross layer and endocarp. Botanically speaking, therefore, the grain is actually a fruit or caryopsis rather than merely a seed, because the pericarp originally constituted the ovary wall within the reproductive section of the wheat flower. The inner bran layers are considered part of the seed proper. They are the testa, the episperm and the aleurone. The testa contains the red-brown pigments which impart the characteristic color to the red wheats. However, the particular color shade in red and white wheat depends not only upon the amount of color pigments in the testa, but also upon the thickness, tint, and transparency of the outer coats or pericarp, and upon the character of the endosperm. The principal color pigments present in the endosperm have been shown to be carotenoid in nature. Markley and Bailey (*144*) have shown xanthophyll to be the main pigment, with carotene present in relatively minor amounts. A number of other unidentified pigments are also obtained when flour is extracted with gasoline. The aleurone layer, which is next to the endosperm, consists of large, heavy-walled, starch-free cells. Although forming the outer layer of the endosperm, it commonly adheres to the perisperm and is removed in milling with the bran. The outer bran layers have a rather tough texture, due to their high content of fiber, which facilitates their removal from the endosperm during milling.

J. A. Shellenberger has measured the thickness of the bran coat of hard

red winter wheat varieties and found the following averages, expressed in microns: Tenmarq, 67.3; Comanche, 68; Red Chief, 70.2; and Chief-kan, 70.4. Shetlar and co-workers (*145*) separated the various layers of wheat bran by a physical and chemical process and subjected them to
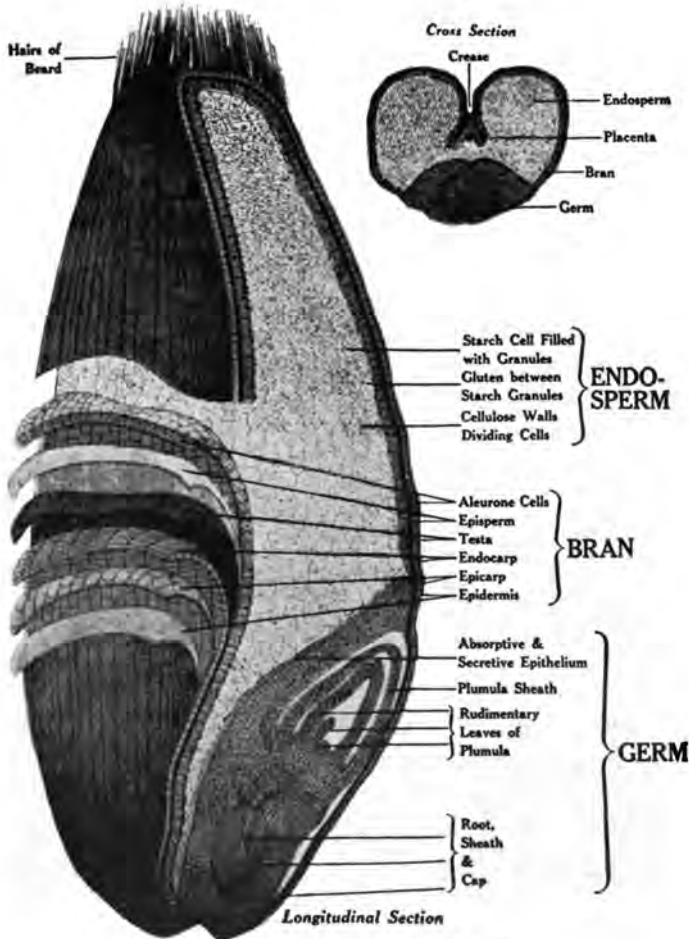
FIG. 37—Structure of wheat kernel.

proximate chemical analysis. They found the total bran to constitute about 14.5 percent of the whole wheat, of which about 3.9 percent was epidermis, 0.9 percent cross layers, 0.6 percent testa, and 9 percent haline and aleurone. The reported proximate chemical composition of the individual bran layers and of the starchy endosperm are summarized in the following table:

TABLE 39. PROXIMATE CHEMICAL COMPOSITION OF BRAN LAYERS

	Ash %	Protein %	Fat %	Cellulose %	Pentosans %
Epidermis..............	1.4	4	1	32	35
Cross layers.............	13	11	0.5	23	30
Testa..................	18	15	0	0	17
Hyaline-Aleurone........	5	35	7	6	30
Endosperm.............	0.7	14	1	0.3	3.5

Because of the quantitative predominance of the hyaline-aleurone portion, this fraction contained about 60 percent of the ash, 90 percent of the protein, 94 percent of the fat, 56 percent of the pentosans, and 29 percent of the cellulose in whole bran based on dry basis.
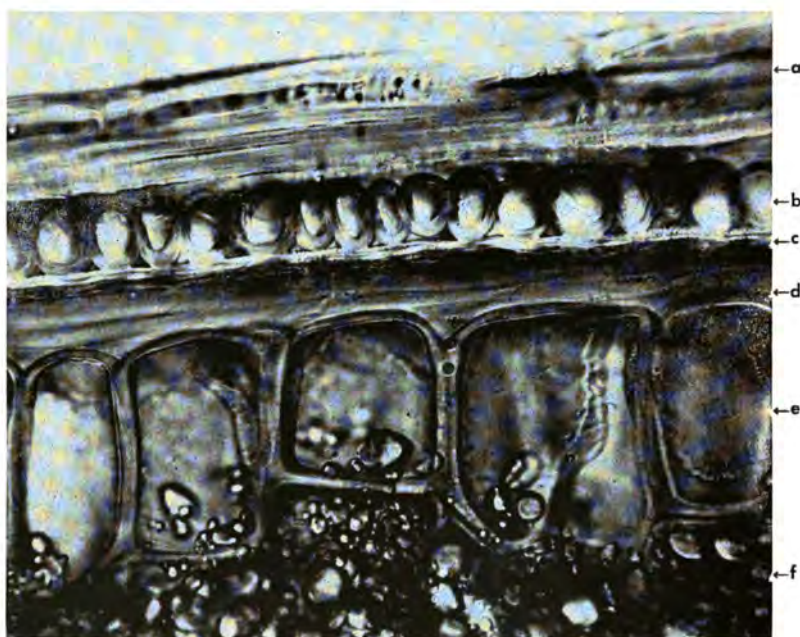
FIG. 38—Longisection of wheat showing the structure of the outer layers of the kernel. (a) Outer pericarp, (b) cross cells, (c) spermoderm, (d) nucellar layer, (e) aleurone, (f) starchy endosperm. (500 × mag.). (*Courtesy Cereal Chemistry.*)

The embryo or germ lies at the base of the grain on its dorsal side and consists of the plumule or stem tip and the radicle or root tip. The plumule, which is enclosed in a sheath, exhibits rudimentary leaves. The rootlet system consists of a tiny root, enclosed in a sheath and provided with a cap at its lower end. The plumule and radicle are connected by the cotyledon which is surrounded by a layer of epithelial cells forming

the so-called scutellum. The function of the scutellum is to secrete enzymes during germination and to absorb and conduct to the growing embryo the food material from the endosperm. Hinton (*146*) has pointed to the exceptionally high thiamine content of the scutellum which, though it comprises only 1.5 percent of the grain, accounts for 59 percent of the grain's total thiamine.

By far the greatest proportion of the wheat berry is comprised by the endosperm which consists chiefly of starch embedded in a matrix of protein. According to Geddes (*136*) wheat kernels contain 2 to 3 percent germ, 13 to 17 percent bran, and 80 to 85 percent endosperm. The bran layers are rich in protein, cellulose, hemicelluloses, and ash; the germ is high in protein, fats, sugar, and ash; the endosperm consists largely of starch and some protein. A detailed description of the structural parts of the wheat grain is given by Fairclough (*147*).

THE MILLING OF WHEAT

The aim of the milling of wheat is to separate as completely as possible the branny covering and germ from the endosperm and to pulverize the latter into flour. To accomplish this objective, the wheat grain is subjected to a series of gradual reductions between iron rolls revolving in opposite directions at different rates of speeds, each reduction being followed by a sifting operation.

Since flours are used for different purposes, such as the production of bread, cake, pie, crackers, doughnuts, etc., the wheats selected for milling must conform to the requirements of these various uses. Thus bread flours are milled from hard wheats, cake and pastry flours from soft wheats, and macaroni flours from durum wheats. Furthermore, there are pronounced variations in quality among varieties within the major wheat classes due to varietal, soil and climatic conditions which require that wheats of different varieties and from different sources be blended to yield flours of proper protein content, diastatic activity and baking behavior. This is a very important operation on the part of the miller since correct blending of wheats forms the basis for the uniformity of a flour's performance in the baking plant.

After the wheat has been properly blended it is subjected to cleaning and tempering prior to its actual grinding. Commercial wheat always contains small percentages of contaminating materials, such as weed seeds and other cereals, dirt, chaff, etc., referred to collectively as dockage. Various methods and devices are used to obtain a complete removal of the foreign material, such as magnetic separators for removing iron and steel objects, screening and forced air drafts for the removal of loose, separable materials, scourers for removing fixed dirt and the brush hairs

of the kernels, washers for removing smut spores and other loosely ad-
hering matter, and special screening machines for the removal of small
stones, seeds of garlic, mustard and cockle, and oats.

The tempering of wheat has for its object the accentuation of the
natural physical characteristics which distinguish the component parts
of the wheat kernel. Milling efficiency is at its maximum only when the
grain is properly conditioned. The branny cover of the kernel is by na-
ture tougher than either the germ or the endosperm, so that the kernel
can be broken up without pronounced reduction of the bran which can
then be separated on the basis of differences in particle size. Bran tough-
ness increases progressively with moisture content. The germ is rather
pliable because of its high oil content and, when it contains the right
amount of moisture, is readily flattened into sizable particles by passage
through narrow-spaced rolls for subsequent removal by bolting. The
endosperm from which the ultimate flour is derived is rendered quite
friable upon addition of the correct percentage of moisture and can then
be fractured into angular particles of various sizes controllable by the
miller. Excessive moisture in the endosperm causes flaking, whereas
insufficient moisture leads to premature pulverization. Tempering of
wheat, therefore, is largely a matter of adjusting the moisture contents
of the kernel's component parts to levels at which separation of bran
and germ from the endosperm occurs most readily. In general the effects
of tempering are primarily physical with practically no chemical changes
occurring during the wheat's treatment. Tempering normally involves
wetting the wheat, followed by storage in tanks for brief periods to allow
for moisture penetration. Some wheats require the application of heat
to bring them into proper condition for milling.

The cleaned and tempered wheat is now subjected to a series of grind-
ing operations, of which the first five or six exert a crushing and shearing
action. Known as breaking and designed primarily to bring about a
far-reaching separation of the tough bran from the friable endosperm,
the first part of the grinding process is carried out on corrugated iron
rolls, called break rolls, which revolve in opposite directions at different
speeds. Proceeding from the first to the fifth or sixth break, the cor-
rugations on the rolls become finer and the setting of the rolls progres-
sively closer. The first break crushes the wheat into coarse particles,
loosens much of the bran and produces but little fine flour, known as
break flour. The crushed material, called stock, then passes to a sifter
or bolter equipped with a series of inclined coarse sieves on top and pro-
gressively finer sieves at the botton which maintain a giratory motion.
Here the separation of the stock proceeds into three general classes of
material according to size: the coarsest fragments, retained on the top

sieves and conveyed subsequently to the second break; the medium sized granular particles consisting chiefly of endosperm and called the middlings; and the finest material passing through the fine silk bottom sieves and called break flour. The same process is repeated at subsequent breaks, yielding flour, middlings, and progressively smaller coarse particles. The stock going to each succeeding break contains less and less endosperm until after the fifth or sixth break the remaining material consists largely of bran flakes.

FIG. 39—Wheat after passage through first breaker rolls. (*Courtesy Wheat Flour Institute*.)

The middlings are composed of endosperm fragments, with some admixture of bran particles and germ. In the sifter they have been graded according to size and the various streams are then combined according to size and degree of refinement. The middlings next pass into the purifier where by means of further sifting and air aspiration they are freed as much as possible from the bran.

After purification, the middlings are gradually ground into flour between smooth rolls, called reduction rolls. This involves a series of reduction processes in which, as in the case of breaking, the smooth rolls are set progressively closer at each succeeding reduction. Each reduction subjects the middlings to a crushing and rubbing action which produces finer middlings and flour, and loosens the adhering bran flakes. The resulting stock then passes through a sifter which effects the separa-

tion of fine flour, reduced middlings and larger bran fragments. The remaining middlings are again graded according to size, purified, and conveyed to the succeeding reduction rolls. It is also at this stage that the germ is separated from the flour by being flattened into flakes upon passage between the rolls and removed by bolting. The reductions are repeated until ultimately most of the endosperm has been converted into flour and the bran separated by the sifters. The final mixture is one of

FIG. 40—Purified middlings. (*Courtesy Wheat Flour Institute.*)

bran, some endosperm and germ which is used for feed and is known as gray shorts.

These series of breaks and reductions give rise to many flour streams which in the case of the larger mills may number as high as thirty. Thus each break produces flour, such as first break flour, second break flour, etc. Each reduction, in turn, produces middling flours. These streams, being derived from different portions of the endosperm and possessing varying degrees of refinement, differ considerably in protein content, ash content, purity from branny material, etc. Beginning with the first middlings separation, which is the most highly refined, the flour contains more and more branny and germ impurities at each successive reduction. The flour obtained from the last reduction, called red dog, is dark in color and high in bran and germ content and largely unsuited for baking purposes. The differences in chemical composition of different flour streams is not entirely due to variations in their germ and bran contents,

but is also accounted for by zonal differences in composition existing within the wheat kernel. Thus it has been found that the protein content of the endosperm increases progressively from the central portion to the zones lying closer to the aleurone layer.

The general trends in average composition of different mill streams as they progress from the head to the tail of the mill are indicated by the data in the following table compiled by B. R. Jacobs and reproduced in part from Geddes (*136*).

TABLE 40. CHEMICAL COMPOSITION OF CERTAIN MILL STREAMS AND BY-PRODUCTS OBTAINED IN WHEAT MILLING

Product	Mois- ture %	Total N %	Fat %	Fiber %	Ash %	Total sugars %
Wheat and mill products						
Wheat.................	10.3	2.05	2.1	—	1.73	2.6
First patent flour........	11.5	1.82	1.0	0.2	0.40	1.3
First clear flour.........	11.0	2.13	1.7	0.2	0.81	1.8
Second clear flour........	10.4	2.33	2.0	0.3	1.34	2.1
Red dog...............	9.2	2.87	5.4	2.4	3.15	6.4
Bran..................	8.8	2.33	4.1	10.8	6.38	5.4
Shorts.................	8.9	2.47	5.2	8.4	4.10	6.0
Germ..................	8.5	4.84	11.9	1.8	4.80	15.1
Flour streams						
First break flour.........	11.8	1.91	1.1	0.2	0.66	1.4
Second break flour.......	11.3	1.99	1.4	0.1	0.56	1.3
Third break flour........	11.5	2.08	1.4	0.1	0.49	1.4
Fourth break flour.......	11.2	2.29	2.2	0.1	0.64	1.5
Fifth break flour........	11.0	2.35	2.6	0.1	1.03	1.6
First middlings flour.....	11.5	1.80	1.0	0.1	0.36	1.2
Third middlings flour....	11.1	1.80	1.1	0.1	0.38	1.4
Fifth middlings flour.....	10.7	1.89	0.9	0.1	0.44	1.5
Seventh middlings flour...	11.1	1.96	1.4	0.1	0.65	2.5
Ninth middlings flour....	10.8	1.84	1.5	0.2	0.61	2.0
First tailings from purifier.	9.8	2.57	5.4	4.4	3.67	4.3

Depending upon which streams are combined to yield the final flour, different commercial flour grades are obtained. If all the streams are combined, a so-called straight flour is obtained. Frequently the more refined streams are kept separate and sold as patent flours while the remaining streams yield so-called clear flours. The most common types of commercial flours are family patent, which contains 65 to 70 percent of the total flour; short patent, with 70 to 80 percent; medium patent, with 80 to 85 percent; and long or standard patent with 90 to 95 percent of the total flour. The remaining clear flours are designated as fancy clear, first clear, and second clear, the degree of refinement decreasing in that

order. The lower grade clear flours are too dark in color and too poor in baking quality to make satisfactory bread flours. Some of the better grades are used for admixture to rye flour, while the lower grades find uses outside the baking industry.

The relationship and the percentages of the various flour grades are given in the chart of Fig. 42. It will be noted that 100 pounds of cleaned wheat will yield 72 pounds of flour and 28 pounds of feed material. When

FIG. 41—Baker's flour, end product of milling. (*Courtesy Wheat Flour Institute.*)

it is considered that wheat, on an average, contains nearly 85 percent of endosperm (*142*) it is evident that a flour yield of 72 percent falls considerably short of the ideal, which would be 85 percent. This failure to obtain all of the endosperm as flour, even in modern milling practice, is accounted for by the fact that part of the outer zones of the endosperm adheres so firmly to the bran that practical separation is not possible with the milling methods in current use.

The various grades of flour differ in their chemical as well as their physical characteristics and require different treatment in the bakery. In Table 40b are shown typical comparative values for various grades of flour milled from the same mix of hard winter wheat (The W. E. Long Company).

The Earle Process. About a decade ago a mining engineer named Theodore Earle observed that when wheat is placed in water and violently agitated, its epidermis or fibrous, indigestible outer coating, be-

came detached and could be floated off. He gained the support of a large chain bakery for this process and was able to develop it commercially. In this process the wheat is mixed with water and passed through ten interconnected tanks called "flotation cells" in which the wheat-water

100 POUNDS OF WHEAT (Swanson, C. O., Wheat and Flour Quality)		
72% OF WHEAT = 100% STRAIGHT, ALL STREAMS		28% OF WHEAT = FEED

FIG. 42—Schematic breakdown showing yields of various milled products from 100 lbs. of cleaned wheat.

TABLE 40B. COMPARATIVE VALUES OF DIFFERENT FLOUR GRADES

Grade of flour	Ash	Protein	Color
Short Patent (65%)	0.39	10.8	100
Standard Patent (95%) containing 65% Short Patent and 30% Clear........................	0.45	11.1	97
Straight (100%) containing 65% Short Patent, 30% Clear and 5% Low Grade................	0.48	11.3	95
Clear (30%)..................................	0.60	12.3	85
Low Grade (5%).............................	0.90	13.0	75

slurry is violently agitated by means of impellers to loosen the outer fibrous hull of the kernels. These hulls, aided by a frothing agent, rise to the top of the cells and are removed by being floated off. The "peeled" wheat is then discharged onto a vibrating screen where most of

the water is removed, further drying being attained by passing the treated wheat through a centrifuge and a rotary dryer. After the wheat has been held for a suitable period in tempering bins it is milled by means of pulverizers of the hammer-mill type instead of the conventional roller mill system. The resultant flour, which is pale golden colored and finely granulated, compares as follows with whole wheat flour (*148*):

TABLE 41.   COMPARATIVE COMPOSITIONS OF WHOLE WHEAT FLOUR
AND EARLE PROCESS FLOUR

	Whole wheat flour %	Earle process flour %
Moisture........................	11.4	11.5
Protein..........................	14.9	15.2
Minerals.........................	1.62	1.53
Crude fat........................	1.82	1.78
Crude fiber......................	2.12	1.66
Carbohydrates...................	68.28	68.14

From these figures it is apparent that the composition of whole wheat flour and of the Earle process flour are very similar in all factors excepting crude fiber which is reduced about 30 percent by the peeling of the wheat. Compared with a fiber content of ordinary patent flour of approximately 0.24-0.28 percent, the 1.66 percent crude fiber found in the Earle process flour is still relatively high. The advantages claimed for the Earle process include better washing of wheat, positive removal of infestation, reduction in tempering time, simplification of the milling process, greater flour yields, better keeping quality of flour, and improved nutritional character of the milled product. The Earle process flour, however, does not produce bread possessing the color and texture which the consumer has come to expect and for this reason the process itself has failed to find general acceptance.

THE COMPOSITION OF WHEAT AND FLOUR

The chemical composition of wheat and its milling products varies over fairly wide limits. Thus protein contents ranging from 6.4 to 21.5 percent have been encountered in American wheats (*140*) and similar relative variations have been observed in the amounts of carbohydrates, lipids, vitamins, minerals, etc. These differences in composition are due to varietal, soil and climatic factors. Normally, however, commercial wheats tend to show much narrower ranges so that proximate average composition data may be safely taken as applying to most wheats intended for milling.

In general, wheats, in common with cereals as a whole, are characterized by a high carbohydrate content which averages approximately 70 percent of the total grain, a relatively low protein content on the order of 9 to 13 percent, and small contents of fat, minerals and vitamins. The carbohydrates of wheat are chiefly starch and cellulose, with small amounts of sugar and pentosans. The proteins include glutenin, gliadin, globulin, leucosin and proteose, of which the first two predominate and account for the characteristic gluten formation. Lipids or fats normally amount to 2 percent of the whole wheat. Commercial bran contains on an average 6 percent oil and germ 12 to 18 percent. Germ oil consists of approximately 15.5 percent of solid acids, 25.5 percent of oleic acid, 52.6

TABLE 42. COMPOSITION OF WHEAT, FLOUR, AND GERM
(Basis 13.5 percent moisture)

Material	Protein	Fat	Ash	Carbohydrates	
				Fiber	Other
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
Wheat:					
All types.............	12.6	1.9	1.6	1.8	68.6
Hard red.............	13.5	2.0	1.6	2.2	67.2
Soft red..............	11.1	1.9	1.7	2.2	69.6
White...............	10.4	1.9	1.7	1.8	70.7
Flour, straight:					
All types.............	11.0	1.1	0.5	0.4	73.5
Hard red.............	11.8	1.2	0.5	0.4	72.6
Soft red..............	10.6	1.0	0.5	0.4	74.0
White...............	9.1	1.0	0.5	0.4	75.5

Source: Proximate Composition of American Food Materials. By Charlotte Chatfield and Georgia Adams, U.S.D.A. Circ. 549, 1940.

percent linoleic acid, and 6.4 percent of linolenic acid in the form of mixed glycerides (*149*). Wheat contains a considerable number of mineral constituents which in their totality make up the ash content of approximately 1.6 to 1.8 percent. The vitamins include the principal members of the B group and vitamin E. In Table 42 is given the composition of wheat, flour, and germ, based on 13.5 percent moisture content of the wheat.

Wheat Proteins. The general character of wheat proteins has been indicated in a preceding chapter. Jones (*150*) has reviewed the different types of proteins found in wheat, their amino acid composition and nutritive properties. He observed that the proteins of the different parts of the wheat kernel, namely the endosperm, germ, and bran, possess certain characteristic differences. Thus the proteins of the endosperm consist chiefly of the prolamin *gliadin* and the glutelin *glutenin,* which are pres-

ent in approximately the same proportions. The amounts of globulin, albumin and proteose found in the endosperm are generally so small as to make it problematical whether they are true constituents of the intact endosperm.

The embryo or germ proteins include the albumin *leucosin*, globulin, and proteose. Leucosin represents approximately 10 percent of the germ and constitutes the greater part of the germ protein. Globulin may be present up to 5 percent. The bran proteins consist of a globulin, albumin, and a prolamin. These proteins differ essentially from the corresponding proteins of the endosperm and germ, both with respect to their elementary analyses and their amino acid composition. Approximately 31 percent of the total bran proteins are comprised of the prolamin, 16 percent of the albumin and 13 percent of the globulin. As Jones points out, the proteins of the endosperm consist almost, if not entirely, of a prolamin and a glutelin, while the embryo proteins consist almost entirely of a globulin and an albumin. The bran proteins, on the other hand, consist of albumin, prolamin and globulin, but no glutenin.

The proteins of the different parts of the wheat kernel differ from each other not only with respect to their types and physical properties, but also with respect to their elementary composition and their amino acid composition as is evident from the next two tables compiled by the same investigator.

TABLE 43. ELEMENTARY COMPOSITION OF WHEAT PROTEINS

	Carbon	Hydrogen	Nitrogen	Sulfur
	%	%	%	%
Prolamins				
Wheat gliadin..............	52.72	6.86	17.66	1.02
Bran prolamin..............	54.25	6.75	15.35	1.35
Albumins				
Leucosin...................	53.01	6.83	16.93	1.30
Bran albumin..............	53.21	6.71	15.42	1.35
Globulins				
Bran globulin..............	53.43	7.40	17.76	0.91
Embryo globulin...........	51.03	6.85	18.39	0.69
Glutelin				
Wheat glutenin.............	52.34	6.83	17.49	1.08

Csonka, by determining the amino acid composition of 74 percent patent flour and whole wheat flour produced from the same samples of wheat, showed the effect of milling upon the distribution of amino acids in milled products. His results are summarized in Table 45 (*151*).

It will be noted that cystine and tryptophane occur in greater amounts in patent flour, while tyrosine and the dibasic amino acids are higher in

TABLE 44. COMPARISON OF THE AMINO ACID COMPOSITION OF THE PROTEINS IN THE DIFFERENT PARTS OF THE WHEAT KERNEL

	Cystine	Arginine	Histi-dine	Lysine	Trypto-phane	Tyro-sine	Basic Nitrogen
	%	%	%	%	%	%	%
Endosperm proteins							
Gliadin.........	2.04	2.97	2.19	0.64	1.09	2.65	1.00
Glutenin........	0.60	4.72	1.76	1.92	1.72	4.78	2.05
Embryo proteins							
Leucosin........	—	5.94	2.83	2.75	—	3.34	3.50
Globulin........	—	—	—	—	—	—	6.83
Bran proteins							
Prolamin........	2.29	4.41	0.84	2.45	1.37	1.80	—
Globulin........	1.52	14.13	2.76	11.84	2.85	2.27	—
Albumin........	3.30	10.04	2.57	4.51	4.76	4.52	—

whole wheat flour. There is, of course, a reduction in proteins when a 74 percent patent flour is milled as is evidenced by the lower percentage of nitrogen. This loss is caused by the removal of shorts and bran, both of which are higher in nitrogen than the patent flour itself.

TABLE 45. THE AMINO ACID AND NITROGEN PERCENTAGES IN MOISTURE-FREE WHOLE WHEAT AND PATENT FLOURS

	Marquis Hard Spring		Tenmarq Hard Winter	
	Whole wheat flour	Patent flour	Whole wheat flour	Patent flour
	%	%	%	%
Amino Acids				
Cystine.....................	0.27	0.31	0.17	0.23
Tryptophane................	0.09	0.12	0.07	0.09
Tyrosine....................	0.87	0.48	0.56	0.49
Arginine....................	0.51	0.41	0.38	0.33
Histidine...................	0.28	0.18	0.12	0.11
Lysine......................	1.51	0.99	1.23	0.86
Total nitrogen.................	3.31	3.02	2.58	2.13

Pence and co-workers (*152*), using principally microbiological assay methods, determined the amino acid composition of glutens prepared by ordinary washing procedures from 17 different flours. They found that the different glutens were essentially uniform in their composition, even though the flours from which they were obtained differed widely with respect to wheat type and source, protein content and baking characteristics. The average minimal value reported by these investigators, expressed as percent of protein of theoretical nitrogen content of 17.5 percent, are: ammonia, 4.5; alanine, 2.2; arginine, 4.7; aspartic acid, 3.7;

cystine plus cysteine, 1.9; glutamic acid, 35.5; glycine, 3.5; histidine, 2.3; isoleucine, 4.6; leucine, 7.6; lysine, 1.8; methionine, 1.9; phenylalanine, 5.4; proline, 12.7; serine, 4.7; threonine, 2.6; tryptophane, 1.1; tyrosine, 3.1; and valine, 4.7.

The Carbohydrates of Wheat. The principal carbohydrates of wheat are starch, dextrins, cellulose, various types of sugars and pentosans. During milling practically all of the cellulose, which forms an important constituent of bran, is removed together with a considerable proportion of pentosans so that the refined flour contains its carbohydrates chiefly as starch, dextrins and sugar, the latter being present in small amounts. The general nature of carbohydrates has been discussed in a previous chapter to which the reader is referred for more detailed information (cf. pp. 3–27). Sugars occur in flour in small but important quantities. Sucrose appears to be present in amounts of 0.5 to 1 percent. Maltose is also present in small amounts, as is glucose or dextrose. Additional sugars which are thought to occur include raffinose and levulose. The initial sugar content of flour is of considerable importance during the first stages of dough fermentation since it is the pre-existing sugars which maintain yeast fermentation until the amylolytic enzymes of flour have had sufficient time to initiate maltose production by means of starch hydrolysis.

Flour also contains small amounts of dextrins which are carbohydrate substances intermediate in size and complexity between the sugars and starch. Kent-Jones and Amos (*153*) give the dextrin content of flour as 0.1 to 0.2 percent. The dextrin content of flour containing malt is considerably increased since the alpha-amylase of the malt splits the large starch molecules into the smaller but still complex dextrins.

Water-soluble pentosans have been shown by Baker and co-workers (*154*) to occur in sound patent bread flours in amounts of approximately 1 percent. Jacobs and Rask (*155*) reported refined flours to contain from 2.25 to 2.80 percent of total pentosans on a dry basis. Pentosans, of which araban and xylan are representative examples, are carbohydrates which on hydrolysis yield pentose sugars such as arabinose and xylose, respectively. The soluble pentosans have been found by Baker and co-workers to form an irreversible gel upon treatment with certain oxidizing agents used as dough improvers. These authors suggest that because of their gelling action the pentosans may play an important role in controlling dough properties. Thus they point out that the rigidity imparted by the gel to the panned dough prevents the coalescence of gas cells in the proof period and hence maintains the cell structure of the bread. The viscosity of pentosans is lowered and their gelling reduced or entirely prevented by solubles from bran, germ, malted grains, or malt,

so that the usual softening of dough produced by the presence of these substances may be due, in part at least, to their effects upon the pentosans. The same authors have also found that the insoluble pentosans are adsorbed upon the surfaces of the starch granules and suggest that the resistance of raw starch to the action of amylase may be due to protection accorded to the starch by the insoluble pentosan layer.

Cellulose is a carbohydrate closely related to starch except that it is very tough, insoluble and indigestible. It is the chief constituent of the cell walls of plants and in wheat is concentrated principally in the bran, which may contain as much as 10 percent of cellulose. The cellulose content of flour—or crude fiber content as it is generally called—is too small to be of significance, being on the order of 0.25 to 0.50 percent according to Swanson (*112*).

The Lipids of Wheat. The lipids or fat-like substances amount to approximately 2 to 3 percent in wheat and one percent in patent flour. Jacobs and Rask (*155*) found that about two-thirds of the ether-extractable fat of the wheat kernel is present in the germ half of the kernel. According to their estimate of the distribution of the total fat in the wheat kernel, the bran and aleurone layer combined contain about one-half, the starchy endosperm about two-fifths, and the germ about 11 percent of the fat. Sullivan (*156*) has reported the distribution of the lipids in the various separations made on a modern mill from hard spring wheat to be approximately as follows:

TABLE 46. DISTRIBUTION OF LIPIDS IN
WHEAT AND CERTAIN MILLED PRODUCTS

	Percent lipids (Alcohol-ether extract) (13.5% moisture basis)
Wheat	3.0
Short patent	1.3
Straight	1.6
Clear	2.7
Low grade	3.2
Bran	6.5
Shorts	7.5
Germ	15.5

About one-third to two-thirds of the germ fat constitute the phosphatide fraction made up of phosphatidic acid, lecithin and cephalin. The unsaponifiable material amounts to 4 to 5 percent. The fatty acids obtained after the removal of the unsaponifiable material from wheat germ oil have been identified by Sullivan and Bailey (*157*) as shown in Table 47.

These data disclose that some 16 percent of the fatty acids are saturated acids and 84 percent are unsaturated acids. Sullivan has found that the lipids of wheat flour contain more volatile fatty acids than those of wheat germ. As is the case with the wheat germ oil, the bulk of the saturated fraction is palmitic acid. The same unsaturated acids, oleic,

TABLE 47.   FATTY ACIDS SEPARATED FROM
WHEAT GERM OIL

	Percent
Palmitic acid	11.76
Stearic acid	3.06
Lignoceric acid	1.18
α-linolenic acid	1.83
β-linolenic acid	1.72
α-linolic acid	22.32
β-linolic acid	29.99
Oleic acid	28.14

linolic, and a small amount of linolenic, are present as in wheat germ, with linolenic the predominating acid of the unsaturated series.

Table 48 gives the constants for wheat germ oil as determined by Jamieson and Baugham (*158*).

TABLE 48.   CONSTANTS OF WHEAT GERM OIL

Specific gravity at 25° C.	0.0269
Refractive index at 20° C.	1.4762
Acid value	7.6
Saponification number	186.5
Iodine number	125.6
Unsaponifiable matter (iodine No. 97.3)	4.7 percent
Saturated acids	13.3 "
Unsaturated acids	75.3 "
Iodine number of unsaturated acids	160.7 "

Wheat fat is subject to rancidity development through oxidation and enzymatic hydrolysis so that in milling an effort is made to reduce as much as possible the fat content of flour and thereby increase the period of storage during which flour will remain sound.

One type of flour deterioration upon prolonged storage is due to the hydrolyzing action of the fat-splitting enzymes, lipases, upon the glycerides of flour, leading to the formation of fatty acids (*159*). Lipase action is favored by high temperature and moisture levels, so that flours stored for long periods under these conditions, i.e., in warm humid climates, deteriorate and lose their baking quality. Doughs made from such deteriorated flours lack extensibility and tear easily. The doughs will not

handle satisfactorily and their gas retention is poor. The volume, flavor and palatability of the bread made from such flours are also inferior. That these adverse effects are attributable to changes in the lipids of the flour may be shown by removing the fatty acids and fat from the deteriorated flour with ethyl ether and adding fresh flour fat in the amount originally present, when the flour will regain its normal baking quality.

The Minerals of Wheat. The mineral matter of wheat and flour is determined by the ashing method which consists of heating a small sample of wheat or flour until all organic matter, such as the starch, sugar, proteins, etc., is burned away, leaving as a residue a white ash. This ash, which may range from approximately 1 to 2 percent of the total wheat, consists of the various inorganic salts and elements that constitute the mineral substances of the grain or flour. Since the ash constituents of wheat are taken from the minerals of the soil, it is evident that both the total mineral content as well as the relative proportions of individual elements depend largely upon the soil, rainfall and other climatic conditions during growth. Thus Greaves (*160*) has determined the mineral content of wheat grown under different conditions and the data shown in Table 49 give the values he found, recalculated to a percentage basis.

TABLE 49. PERCENTAGE OF MINERAL IN WHEAT GROWN UNDER
VARYING CONDITIONS

Treatment	Percent
No irrigation water	1.56
35 inches irrigation water	2.28
Spring wheat (average of 7 varieties over 8 years)	1.60
Winter wheat (average of 17 varieties over 8 years)	1.40
Wheat grown in 1934 (dry season)	1.09
Wheat grown in 1923	1.58
No manure, stubble burned	1.52
Green manure	1.71

The minerals of wheat are not evenly distributed among the individual parts of the kernel but occur in much higher concentrations in the bran portion than in the endosperm portion. Analyses have shown that bran, on the whole, contains approximately 20 times as much ash as does the endosperm, the actual approximate values being from 5.5 to 8 percent ash for bran and 0.28 to 0.39 percent for endosperm. This great differential in ash content affords a useful means for checking the efficiency of the milling process since the ash content of flour over and above the natural mineral content of the endosperm is derived from bran, so that an excessively high ash content is indicative of relatively high admixtures of bran to the flour such as occur with low grade flours. In an average soft wheat the ash content of the endosperm is about 0.32 per-

cent and of the bran about 5.8 percent. Using these values as a basis, Kline (*161*) has set up the following table to indicate the percentage of bran in flour made from such wheat.

TABLE 50.   RELATION OF FLOUR ASH TO BRAN
CONTENT

Percentage of ash in flour	Percentage of shorts and bran in flour
0.36	0.75
0.40	1.48
0.46	2.75
0.50	3.29
0.60	5.11
0.80	10.00

It should be emphasized at this point that there exists no direct relationship between the ash content of flour and its baking quality. In general, soft wheat flours contain a lower ash content than do hard wheat flours, yet the latter possess superior baking characteristics for bread baking. On the other hand, low grade flours containing high amounts of bran will not perform satisfactorily.

Analyses have shown the ash of wheat to consist of a considerable number of elements. Those present in largest amounts are potassium, phosphorus, sulfur, magnesium, chlorine, and calcium. Other elements which occur in smaller amounts are silicon, iron, manganese, zinc, copper, nickel, cobalt, selenium, aluminum, arsenic, iodine, bromine, fluorine, vanadium, and boron. Sullivan (*162*) has compiled average analyses of the elements present in wheat, flour, and bread, which are reproduced in Tables 51 and 52.

TABLE 51.   AN AVERAGE ANALYSIS OF THE ELEMENTS FOUND IN GREATEST
AMOUNT IN WHEAT, FLOUR, AND BREAD

Constituent	Wheat	Patent flour	Bread[2]
	percent[1]	percent	percent
Total ash............................	1.86	0.45	2.77
Potassium........................	.571	.168	.200
Phosphorus......................	.428	.113	.140
Sulfur............................	.194	.165	.192
Magnesium......................	.173	.029	.040
Chlorine.........................	.055	.051	1.005
Calcium..........................	.048	.016	.080
Sodium..........................	.009	.003	.660
Silicon...........................	.006	.005	.005

[1] Calculated to dry basis
[2] Includes minerals added in formula

The Vitamins of Wheat and Flour. The principal vitamins present in wheat and its milled products are the B complex vitamins and tocopherol, or vitamin E. Of the other recognized vitamins, vitamin A is present in small amounts, while the others are either completely absent or occur only in insignificant amounts.

A voluminous literature has accumulated in recent years dealing with methods of vitamin assay and vitamin contents in wheat. An excellent

TABLE 52. AN AVERAGE ANALYSIS OF THE ELEMENTS FOUND IN LESSER AMOUNT IN WHEAT, FLOUR, AND BREAD

Constituent	Wheat	Patent flour	Bread
	p.p.m.	p.p.m.	p.p.m.
Zinc..	100	40	50
Nickel..	35	—	—
Iron..	31	8	10
Manganese......................................	24	3	8
Boron..	16	4	3
Copper...	6	2	5
Aluminum......................................	3	0.6	—
Bromine..	2	1	1
Iodine...	0.006	0.004	—
Arsenic..	0.1	0.01	—
Cobalt...	0.01	—	—
Fluorine, vanadium, selenium, etc. present			

and detailed summary of published studies up to and including 1943 has been compiled by C. H. Bailey (*163*).

Until relatively recently, main attention has centered upon the thiamine content of wheat and wheat products. Numerous samples of different varieties of wheat have been analyzed and their thiamine content determined. In general, it has been found that the thiamine content of wheat is influenced by both variety and environmental conditions. The average value accepted by the Council on Foods and Nutrition of the American Medical Association for whole wheat is 2.04 mg. thiamine per pound, and 0.23 mg. per pound for white patent flour. Of course, values considerably above and below these averages have been reported in the literature. On the whole, spring wheat and hard winter wheat varieties have somewhat higher values (in the range of 2.25 to 2.55 mg. per pound), while soft wheats have a lower thiamine content (approximately 1.60 mg. per pound). Representative thiamine values of various market classes of wheat are reported by Downs and Cathcart (*164*) and are summarized in the following table, with the original figures recalculated on a mg./lb. basis:

TABLE 53.   AVERAGE THIAMINE CONTENT OF MARKET CLASSES OF
WHEAT

Market class	No. of samples	Average B₁ content mg./lb.
Spring	10	2.92
Hard winter	70	3.24
Soft winter	17	2.79
Western red	2	3.10
White wheat, including "club"	13	2.70
Durum	9	3.28

Thiamine is not uniformly distributed in the wheat kernel, tending to be concentrated in the scutellum and adjacent epithelial layers, less so in the germ and bran portions, and being lowest in concentration in the endosperm portions. As a result, mill products comprising different parts of the kernel show marked variations in their thiamine content as is brought out in the following table by Sherwood (*165*) in which the values represent averages of three sets of mill products from one commercial mill.

TABLE 54.   THIAMINE DISTRIBUTION IN MILLED WHEAT PRODUCTS

Sample	Milling yield, % of cleaned wheat	Thiamine content	
		Mg. per pound	Percent of total thiamine in wheat
Patent flour	63.0	0.31	8.0
First clear	7.0	1.36	3.9
Second clear	4.5	5.61	10.0
Red dog	4.0	13.45	22.0
Germ	0.2	10.40	0.9
Shorts	12.3	7.89	39.6
Bran	9.0	4.25	15.6
Cleaned wheat	100.0	2.28	100.0

It is apparent from the above values that in order to appreciably increase the thiamine content of white flour, the extraction would have to be extended to include at least the red dog flour, in which case a product of 78.5 percent extraction would result, containing approximately half of the thiamine content of whole wheat.

The riboflavin content of wheats and their milled products have been reported by many investigators. The Council on Foods and Nutrition of the American Medical Association has accepted an average value of 1.13 mg. of riboflavin per pound of whole wheat and of 0.18 mg. per pound of white flour. The value for whole wheat appears to be rather

high in the light of data published subsequently. The riboflavin content of wheat does not seem to be markedly affected by environmental factors, but does vary with variety. This is indicated by the following values for different wheats as obtained by Andrews, Boyd and Terry (*166*) and recalculated on a mg./lb. basis. A difference of 20 percent was consistently found between Marquis wheat, which had the highest riboflavin content, and Rival wheat, the variety with the lowest riboflavin content.

TABLE 55. RIBOFLAVIN CONTENT OF
DIFFERENT WHEAT VARIETIES

Variety	Average riboflavin content mg./lb.
Marquis	0.59
Pilot	0.56
Thatcher	0.54
Ceres	0.54
Renown	0.53
Rival	0.48

The same authors also determined the riboflavin content of the milled products of wheat. Here, as in the case of thiamine, the results show that riboflavin is not uniformly distributed in the wheat kernel but tends to be concentrated in those portions which constitute the red dog flour, shorts and bran. The following table, by Andrews, Boyd and Terry

TABLE 56. RIBOFLAVIN AND THIAMINE CONTENT OF MILLED WHEAT PRODUCTS

Mill product	Percentage of wheat	Thiamine mg./lb.	Riboflavin mg./lb.	Percentage of total vitamin of wheat in each mill product	
				Thiamine	Riboflavin
Wheat	100.0	1.98	0.45	100.0	100.0
Patent flour	65.0	0.39	0.15	12.1	20.5
First clear flour	5.5	1.53	0.28	4.1	3.2
2nd clear flour	4.5	8.40	0.83	18.5	7.7
Red dog	4.0	12.19	1.71	24.0	14.4
Shorts	12.5	4.43	1.66	27.2	32.5
Bran	8.5	3.38	1.66	14.1	22.0

(*167*), includes also the thiamine content of the same wheat samples and compares the relative variability of the two vitamins in the various mill products. The original values have been recalculated on a mg./lb. basis.

Less consistent information is available at present concerning the niacin content of wheat and its milled products than is the case with

the two preceding vitamins. This is due to the fact that the currently used chemical and microbiological methods yield variable results. Reported values for wheat range from 6.0 mg. per pound to as high as 47 mg. per pound. The average appears to approximate 25 mg. Teply and Elvehjem (quoted by C. H. Bailey (*163*)) determined the niacin content of hard and soft wheats and found the following values:

	mg./lb.
Hard spring wheat................	24.75-34.65
Soft red winter wheat..............	23.40-30.15
Hard red winter wheat............	22.95
Soft white spring wheat............	23.85

The niacin distribution in the wheat kernel differs markedly from that of the other members of the vitamin B complex. Thus whereas the germ is a relatively rich source of thiamine and riboflavin, only approximately 0.2 percent of the total niacin in the wheat is found in the germ. About 56 percent of the niacin is located in the bran and 18 percent in the shorts. Increasing the flour extraction from 70 to 80 percent would result in only a very slight increase in the niacin content of the flour.

The pyridoxine, or vitamin B_6, content of wheat has been reported to be approximately 1.8 mg. to 2.25 mg. per pound. This vitamin appears to be rather evenly distributed throughout the wheat kernel, with none of the various sections of the berry containing a preponderant concentration.

Pantothenic acid occurs in wheat to the extent of 4.2 to 7.7 mg. per pound. White patent flour has been shown to contain about 2.5 mg. per pound, indicating that the vitamin is not evenly distributed in the wheat kernel, but occurs in higher concentrations in the lower quality fractions.

Tocopherol, or vitamin E, occurs in wheat to the extent of approximately 26 mg. per pound. More than half of the tocopherol content of wheat is concentrated in the germ oil, the remainder occurring mainly in the pericarp or adjacent tissues surrounding the germ and endosperm. The endosperm itself appears to be practically devoid of tocopherol.

Binnington and Andrews (*168*) have determined the distribution of vitamin E in the milled products of hard wheat, obtaining the results recorded in Table 57.

Enzymes in Wheat and Flour. The general nature of enzymes and their modes of action have been discussed in a preceding chapter. Although cereal chemists have devoted their major attention to the starch hydrolyzing amylases and the protein-splitting proteinases, sight should not be lost of the fact that wheat and flour contain a large number of other enzymes whose functions in breadmaking, though less thoroughly

understood, are nevertheless significant. Thus the hemicelluloses, which are made up of pentosans, and the wheat gums undergo enzymatic modifications, according to Luers (*169*), to yield fermentable and unfermentable sugars which participate in the browning reaction occurring in the baking crust by forming melanoidins with amino acids. The esterases are of significance insofar as they liberate inorganic compounds, particularly phosphoric acid, from their organic combinations. These inorganic compounds serve as buffer substances on the one hand and as yeast food on the other. Approximately 90 percent of the phosphorus present in flour is organically bound and a considerable part of this is converted

TABLE 57. MILL YIELD, OIL CONTENT, AND TOCOPHEROL CONTENT AND DISTRIBUTION
IN HARD WHEAT MILLED PRODUCTS

| Sample | Mill Yield | Oil | Tocopherol in 100 g | | |
			in oil	mill product	distri- bution
	%	%	%	mg	% of total
Patent flour........	60.3	0.83	0.003	0.03	2.0
1st clear flour.......	9.4	1.78	0.082	1.46	17.4
2nd clear flour......	4.1	4.16	0.069	2.87	14.8
Red dog...........	2.7	5.83	0.099	5.77	20.0
Shorts.............	9.3	4.41	0.072	3.18	37.6
Bran..............	14.0	2.97	0.012	0.30	6.3
Germ..............	0.1	8.90	0.178	15.84	1.9
Whole wheat.......	—	1.54	0.059	0.91	—

into inorganic phosphorus during dough fermentation by such phosphatases as phytase, glycerophosphatase, saccharophosphatase and nucleotidase. The presence of inorganic phosphates and of yeast phosphorylases is essential for the formation of the various hexose-phosphoric acid esters which occur as intermediary stages in sugar fermentation. Additional enzymes found in flour are the desmolases, such as catalase, peroxidase, reductases and oxidases, all of which enter into important oxidation-reduction reactions. Undoubtedly as the actions of these enzymes become more clearly understood and their role in breadmaking more completely clarified they will assume greater significance in baking technology than is at present accorded to them.

FEDERAL FLOUR STANDARDS

The Federal Security Agency of the Food and Drug Administration has established definitions and standards of identity for flour and related products, effective January 1, 1942 (*170*). These standards provide in each case that the product be made from cleaned wheat other than durum

wheat and red durum wheat and that the moisture content must not exceed 15 percent as determined by the official vacuum oven method of the Association of Official Agricultural Chemists. Other provisions pertaining more specifically to the individual products are as follows:

Flour, white flour, wheat flour, plain flour is the product obtained by grinding and bolting wheat and which is freed from bran and germ to such an extent that the percentage of ash, calculated on a moisture-free basis, is not more than one-twentieth of the percent of protein and 0.35. One of the cloths through which the flour is bolted has openings not larger than those of woven wire cloth designated "149 micron (No. 100)" in Table 1 of "Standard Specifications for Sieves," published March 1, 1940, in L.C. 584 of the U. S. Department of Commerce, National Bureau of Standards. To compensate for any natural deficiency of enzymes, malted wheat, malted wheat flour, malted barley flour, or any combination of two or more of these, may be added but the addition of malted barley flour may not exceed 0.25 percent. One or any combination of two or more of the following optional bleaching and/or aging ingredients may be added in a quantity not more than sufficient for bleaching and artificial aging effect: (1) oxides of nitrogen, (2) chlorine, (3) nitrosyl chloride, (4) nitrogen trichloride (the use of nitrogen trichloride, known commercially as "Agene" has been discontinued as of Aug. 1, 1949 as a result of findings which indicate that this bleaching agent combines with wheat protein to form a substance which has proved toxic to certain animals), (5) benzoyl peroxide mixed with not more than six parts by weight of a mixture of either potassium alum or calcium sulfate and magnesium carbonate. When any optional bleaching agent is used, the flour must be labeled "bleached."

Enriched flour must conform to the above provisions except that it contains in each pound not less than 2.0 mg. and not more than 2.5 mg. of thiamine, not less than 1.2 and not more than 1.5 mg. of riboflavin, not less than 16.0 mg. and not more than 20 mg. of niacin or niacin amide, not less than 13.0 mg. and not more than 16.5 mg. of iron. It may also contain as optional ingredients not less than 250 U.S.P. units and not more than 1,000 U.S.P. units of vitamin D, and not less than 500 mg. and not more than 625 mg. of calcium. It may also contain up to 5 percent by weight of wheat germ or partly defatted wheat germ.

Bromated flour must conform to the provisions for white flour except that potassium bromate may be added in a quantity not exceeding 50 p.p.m. to flours whose baking qualities are improved by such addition.

Enriched bromated flour must conform to the provisions for enriched white flour except that potassium bromate may be added up to 50 p.p.m. of the finished bromated flour.

Self-rising flour, self-rising white flour, self-rising wheat flour conforms to the standard and definition of white flour except that it contains additions of sodium bicarbonate, the acid-reacting substances monocalcium phosphate or sodium acid pyrophosphate or both, and salt. The acid-reacting substance is added in sufficient quantity to neutralize the sodium bicarbonate. The self-rising flour must contain enough of the leavening agents to evolve not less than 0.5 percent of its weight of carbon dioxide. The combined weight of leavening agents may not exceed 4.5 parts per 100 parts of flour.

Enriched self-rising flour must conform to the definition and standard prescribed for self-rising flour except that it contains thiamine, riboflavin, niacin and iron in the amounts specified for enriched flour and not less than 500 mg. and not more than 1,500 mg. of calcium. It may also contain vitamin D as an optional ingredient and germ or partly defatted germ up to 5 percent by weight.

Phosphated flour, phosphated white flour, phosphated wheat flour must conform to the definition and standard prescribed for flour except that monocalcium phosphate is added in a quantity not more than 0.75 percent of the weight of the finished phosphated flour.

Whole wheat flour, graham flour, entire wheat flour is a whole wheat product ground so that not less than 90 percent passes through a No. 8 sieve and not less than 50 percent passes through a No. 20 sieve. It may contain malted wheat, malted wheat flour (not exceeding 0.5 percent), malted barley flour (not exceeding 0.25 percent), or any combination of two or more of these to compensate for any natural deficiency of enzymes. It may be bleached and aged with chlorine, or a mixture of nitrosyl chloride and chlorine.

Bromated whole wheat flour conforms to the definition and standard for whole wheat flour except that it contains potassium bromate in a quantity not exceeding 75 p.p.m. of the finished bromated product.

Crushed wheat, coarse ground wheat is a whole wheat product crushed to such fineness that 40 percent or more passes through a No. 8 sieve and less than 50 percent passes through a No. 20 sieve.

Cracked wheat is a whole wheat product obtained by so cracking or cutting into angular fragments cleaned wheat that not less than 90 percent passes through a No. 8 sieve and not more than 20 percent passes through a No. 20 sieve.

Farina is coarsely ground endosperm freed from bran and germ to an ash content not exceeding 0.6 percent. Its granulation is such that it passes through a No. 20 sieve, but not more than 3 percent passes through a No. 100 sieve.

Enriched farina conforms to the definition and standard of farina ex-

cept that it contains in each pound a minimum of 1.66 mg. of thiamine, 1.2 mg. of riboflavin, 6 mg. of niacin and 6 mg. of iron. A minimum of 250 U.S.P. units of vitamin D and of 500 mg. of calcium may be added optionally. It may contain a maximum of 8 percent of wheat germ or partly defatted germ.

BLEACHING OF FLOUR

Freshly milled flour obtained by the modern roller mill process possesses a yellowish tint imparted to it by certain carotinoid pigments which are present in the endosperm. The principal color pigment has been found to be xanthophyll, with minor amounts of carotene and other unidentified color pigments present in minute amounts. These carotinoids are changed into colorless compounds upon oxidation so that the flour assumes a nearly pure white color. Formerly, this oxidation was permitted to proceed naturally by storing the flour for several months, thereby allowing the oxygen of the air to react slowly with the color pigments. During this storage or "aging" period the flour undergoes a process of autoxidation which, in addition to color removal, results in a marked improvement of its baking characteristics.

Early investigations into the reactions which occur in the storing of flour led to the development of artificial bleaching which makes possible the removal of color within a number of minutes instead of weeks. Furthermore a number of bleaching agents were made available which also matured the flour so that the artificially bleached product was in all respects comparable to flour that had been naturally aged over a period of several months. At present there are about four bleaching agents in general use, namely nitrogen peroxide, nitrogen trichloride, chlorine with nitrosyl, and benzoyl peroxide. The first three are gases, while the last named is a solid. In practice the freshly milled flour is brought into intimate contact with the bleaching agent in a special mixing unit known as an agitator.

Nitrogen peroxide (N_2O_4) is the active agent in the so-called Alsop process which was first introduced into American mills in 1904. It was almost universally employed for nearly twenty years, only to lose favor with the appearance of other bleaches so that at present its use is greatly restricted. Nitrogen peroxide is made by passing air through an electric flaming arc which causes the atmospheric oxygen to unite with the nitrogen to form the nitrogen peroxide. By properly adjusting the volume and electric current the amount of bleach can be accurately controlled.

The Agene process made use of nitrogen trichloride (NCl_3), a gas produced by passing chlorine through a solution of ammonium chloride. Agene matures the flour in addition to its bleaching action. After an

ingenious metering device was made available which permitted the accurate addition of this powerful agent to flour, its popularity increased to a point where during the past twenty-five years approximately 90 percent of all bleached flour in the United States was treated with this agent. In 1946 Sir Edward Mellanby of England observed that when Agene-treated flour was fed to dogs it produced in the animal a disorder known as canine hysteria or running fits. This observation, confirmed by other scientists, led to a re-investigation of the possible toxic effects of nitrogen trichloride. Extensive studies carried out in the University of Wisconsin by Elvehjem and co-workers (*171*) showed rather conclusively (1) that human beings fed Agenized proteins at a rate of 20 times the normal intake over prolonged periods of time did not exhibit the slightest evidence of harm when examined by the most sensitive tests available, and (2) that dogs, the animal which shows the highest degree of sensitivity toward Agene treated flour, remained completely normal when fed a ration for six to eight months which contained an amount of flour approximately equal to that used in the average American diet. Despite these favorable results, the criticism leveled against the use of nitrogen trichloride had reached such proportions that the milling industry in 1948 decided to abandon the Agene treatment of flour in favor of some alternative treatment. The Food and Drug Administration ruled toward the end of 1948 that the use of Agene was to be discontinued effective August 1, 1949, and that chlorine dioxide would be acceptable as an alternative bleaching agent. Practical results with chlorine dioxide, known commercially as Dyox, indicate that its effect is comparable to that of Agene (*171a*). Numerous investigators, including Newell and co-workers (*171b*), have carried out extensive feeding tests with chlorine dioxide treated flour, using both animal and human subjects. In no instance were any untoward effects observed even on consumption of large amounts of wheat flour and wheat gluten treated with high levels of chlorine dioxide.

The Beta Chlora process employs chlorine gas to which 0.5 to 5 percent of nitrosyl chloride (NOCl) has been added. This mixture has a powerful mellowing action upon the gluten proteins of flour and must therefore be carefully metered. Its most general use is in the treatment of soft wheat flours designed for cake making, and of hard wheat flours exhibiting an excessively long fermentation period.

Benzoyl peroxide ($C_6H_5CO)O_2$, also known as Novadelox, is the only bleach used to any extent in solid form, being normally mixed with a neutral carrier, such as calcium phosphate, to reduce its inflammability. It is an effective bleaching agent with little action on the flour proteins.

Most of the currently used bleaching agents also produce an improv-

ing action on the baking behavior of the flour. In some instances this effect is accentuated by the addition of certain oxidizing agents, of which potassium bromate is the most extensively used. According to Federal flour standards, potassium bromate may be added to flours requiring such improving treatment up to a maximum of 50 p.p.m. The belief has at times been expressed that the effects of such bleaching agents as Agene, Novadelox and Beta Chlora, which also produce a discernible improvement in the baking quality of the treated flour are similar to that obtained with potassium bromate. Harris and Bayfield (*172*), however, have shown that very definite differences exist between bleaching and bromate action and that these terms are therefore not synonymous. Bleaching agents have a marked effect upon the coloring matter of flour, principally carotene, making it colorless. They thereby produce a whiter crumb and in addition bring about a noticeable improvement in the volume, grain and texture of the bread. Potassium bromate, on the other hand, is without effect upon crumb color. Furthermore, the increase in loaf volume and the improvement in grain and texture are more pronounced in the case of potassium bromate than when bleaching agents solely are used.

The use of bleaching agents should not be misconstrued as an attempt on the part of millers to conceal a possible inferiority of the product. The color of flour is governed by three factors: granulation, carotinoid pigments, and bran particles. The coarser the granulation, the less bright will be the appearance of the flour. Granulation is entirely a matter of the setting of reduction rolls and remains unaffected by bleaching. Low grade flours derive their darker color principally from their high content of bran particles. The coloring matter of bran, however, is not affected by bleaching agents so that any improvement of color by bleaching is due solely to the effect upon the carotenoids which are naturally present in the endosperm. Bleaching will improve the baking quality of lower grade flours without, however, concealing their true character.

FLOUR STRENGTH

The concept of flour strength or flour quality has been discussed recently by Harris (*173*) who also reviewed the pertinent literature. Flour strength is very difficult to define concisely. This is due largely to the fact that flour quality is indicated by a variety of physical characteristics of the dough, none of which serves as an adequate index by itself or is independent of other variables. Thus different physical testing methods, different test formulas and different dough treatments, when applied to the same flour, will yield results which may lead to widely divergent conclusions as to the flour's quality. Furthermore, the purpose to which

a flour is to be put must enter importantly into any evaluation of its quality. The marked distinction between a soft cake flour and a hard bread flour is clearly recognized by every baker. On the other hand, a baker may be less certain in distinguishing between the requisite properties of flours designed for the production of white pan bread as against hearth breads. Thus a flour which is eminently suitable for making a pan loaf may prove less satisfactory for a hearth loaf. Such a flour would therefore be adjudged as of good quality in one case and of lesser quality in the other.

Various definitions of flour strength have been proposed. One of the earliest is that of Humphries (*174*) according to which "a strong wheat is one which yields flour capable of making large, well-piled loaves." The resultant loaves must therefore not only be large, but possess also a smooth silky texture as implied by the word "pile," a term borrowed from the textile industry. A flour giving a large volume but coarse texture would, according to this definition, not be considered a strong flour. Humphries' definition was subsequently amended by Kent-Jones (*175*) to read, "Strength is the ability of flour to be converted into large, well-piled loaves, provided any deficiency in the rate of gas production in the dough stage is supplemented in a suitable manner," so as not to disqualify flours having sufficient gluten of good quality but lacking in diastatic activity. These latter flours will yield satisfactory loaves after they have been properly treated with diastatic supplements. Bailey (*142*) found the concept of flour strength implied by the modified definition to be substantially complete but felt that it could be stated in more definite terms. He suggested that the strength of flour is determined by the ratio between (a) the rate of carbon dioxide production in the fermenting dough and (b) the rate of loss of the gas from the fermenting dough. Gas production is, of course, closely associated with the sugar level in the dough which in turn depends upon the flour's diastatic activity and content of available starch. Gas loss, or its converse, gas retention, is on the other hand related to the quantity and quality of gluten and the manner in which it develops during dough mixing and fermentation.

Blish (*176*) made a distinction between baking quality and baking strength. Baking quality he related to inherent or potential possibilities of a flour, while baking strength implied both quality and a certain degree of tolerance to variations in baking treatment. Accordingly, a given flour can possess quality without strength, but not strength without quality. A flour which lacks strength, i.e., a weak flour, can under circumstances be given such special treatment that a large loaf results, whereas under normal or unfavorable treatment it will fail to give good results.

Flours of this type usually possess high quality gluten proteins at a marginal level. On the other hand, certain high protein flours may possess too much strength to yield satisfactory results without special treatment designed to mellow and modify the tough gluten. In this instance, of course, the above implied meaning of strength would require qualification, since these excessively strong flours also require special treatment. Harris (*173*) suggests in this connection that the practice of blending flours with a specified quantity of starch or soft winter wheat of low protein content and baking the blends probably yields as true a picture of strength as can be secured, particularly for hard red spring wheats.

After Osborne had shown gluten to consist of the two proteins gliadin and glutenin, a number of investigators attempted to establish the optimum ratio of the wheat proteins in relation to baking strength. Snyder (*177*) thought that a well-balanced gluten was composed of 55 to 65 percent gliadin and 45-35 percent glutenin. Blish (*178*) found the gliadin-glutenin ratio to be nearly constant in strong and weak flours and also failed to observe any essential differences in the chemical constitution of the proteins of wheat flour. Grewe and Bailey (*43*), failing to detect any significant variation in the ratio of glutenin to crude gluten or of glutenin to gliadin, concluded that this ratio was unreliable as a means for distinguishing between various types of flour. Harris and Bailey (*179*) found that the quantity of gliadin obtained by thermal fractionation from a given quantity of wet gluten washed from various flours was significantly and positively correlated with crude protein and loaf volume. This was not the case in the instance of glutenin and mesonin, the other two fractions investigated. From the above it is apparent that little agreement exists between the various investigators regarding the value of the ratios of wheat protein fractions as indicators of the baking strength of flour.

Blish and Sandstedt (*180*) felt that the protein content of flour was the only true index of baking strength and that variations in gluten quality could be compensated for by suitable adjustments in baking treatment. The difficulty here is, however, that of measuring by objective tests the very elusive properties designated as "gluten quality." Many attempts have been made in the past to obtain some definite measure of the physical properties of gluten from different flours. Wood (*181*) and Wood and Hardy (*182*) first recognized the importance of environment upon the physical behavior of gluten and with this observation laid the groundwork for the modern theories of colloidal chemistry as applied to gluten properties. Upson and Calvin (*183, 184*) studied the hydration of gluten in dilute acid solutions and concluded that the amount of water imbibed by gluten was primarily a function of the presence of acids in

the medium. Gortner and Doherty (*185*), on the other hand, found that glutens from strong flours had a greater hydration capacity than glutens from weak flours, when investigated by the method of Upson and Calvin. Gortner and Doherty attributed the difference between a strong and a weak gluten to the more perfect colloidal gel with highly pronounced physico-chemical properties formed by the strong gluten as compared with a colloidal gel formed by weak gluten in which these properties are less pronounced. Swanson (*31*) states that strength or weakness from the standpoint of inherent gluten structure is determined by wheat variety and by conditions of growth, ripening and storage. An excellent review of the investigational work on viscosity, gluten, dough, flour proteins and fats and lipoids in relation to flour strength has been provided by Amos and Kent-Jones (*153*).

FLOUR ABSORPTION

The importance of absorption as a factor in quality control has long been recognized and is the subject of a considerable volume of literature. The correct determination of the optimum absorption of flour is inherently difficult because it has thus far not been possible to express it as a single value, i.e., a value that would be generally applicable. This becomes readily apparent from the very definition of the term "flour absorption" which is taken to mean "the amount of liquid that is required to give a dough with proper handling and machining properties and that will produce the best final baked product." What constitutes proper handling and machining properties depends considerably upon the particular conditions that exist in individual baking plants. A large element of subjective judgment is further involved in any decision as to what constitutes the best final baked product. Thus a given absorption value found to yield optimum results in a highly mechanized bakery will seldom give equally satisfactory results in a hand shop.

There are three general methods that have been used to calculate absorption: (1) The fully corrected method, basis 15 percent moisture; (2) the dry matter corrected method, basis 15 percent moisture; and (3) the "as is" basis. The great range in values that can be obtained with a single flour by the use of these different methods has been rather strikingly illustrated by Merritt and Stamberg (*186*). These authors have calculated the absorption value of the same flour containing 12 percent moisture by these three methods to show how three widely divergent values can be obtained, only one of which can be correct.

In the fully corrected method, 15 percent basis, the amount of water required to bring the moisture content of flour from the "as is" basis to 15 percent does not constitute part of absorption. Thus if a flour of 12

percent is taken as an example, 100 g. of the flour contain 88 g. of dry matter. To convert such a flour to a 15 percent moisture basis, i.e., with 85 g. of dry matter, only 96.6 of the flour is used and one must add 3.4 g. of water to make the total equal 100 g. All additional water required in making the dough is then called the absorption of 100 g. of flour, basis 15 percent. If 58 g. of water are used beyond the 3.4 g. already needed for flour weight correction, then 58 is the percentage of absorption. By the use of this method, the absorption value of the flour remains constant regardless of the moisture content of the original flour.

In the second dry matter corrected method, 15 percent moisture basis, the amount of water required for the correction of flour weight is considered part of the absorption value. Using the same flour as before, the amount of water added would be 3.4 g. plus 58 g. to give a total of 61.4 g., and 61.4 is then given as the percentage of absorption. With this method, the absorption of the same flour will vary with differing original moisture contents.

With the third method, using the "as is" basis, the absorption of the flour used above would be 63.7 percent, which is the result of the following calculation: (61.4/96.6) × 100. Here, of course, the original moisture content of the flour tends to distort the actual absorption value the most.

Merritt and Stamberg have illustrated in the following table how the difference in values obtained by these three methods depends on the moisture content of the flour, using as an example a hypothetical flour with an absorption value of 56.

TABLE 58.   FLOUR ABSORPTION BY DIFFERENT METHODS OF CALCULATION

Flour	Moisture content of flour	Absorption, 15% moisture basis, fully corrected	Absorption, 15% moisture basis, dry matter corrected	Absorption on "as is" basis
	%	%	%	%
1................	8.4	56.0	63.3	68.3
2................	10.1	56.0	61.5	65.5
3................	11.0	56.0	60.5	63.4
4................	12.0	56.0	59.4	61.5
5................	14.0	56.0	57.1	57.8

It will be noted that with the flour of low moisture content the absorption values show a relatively wide range, whereas when the moisture content of the flour is high, the difference diminishes markedly. The authors suggest that the use of all three methods perhaps accounts for the rather wide range of absorption values occurring in the literature, and recommend the use of the fully corrected method since the result-

ing data could then be used to find the correct ratio of liquid to dry matter.

The magnitude of actual flour absorption is to a large degree dependent upon the protein content of the flour. Thus Merritt and Stamberg found that absorption, as determined by the farinograph, increased by about 1.5 percent for each 1 percent increase in the protein of the flour. The relation between protein content and absorption is shown more clearly by the figures in the following table (*187*):

TABLE 59.   RELATION OF PROTEIN CONTENT TO
FLOUR ABSORPTION

Variety	Protein %	Absorption %
Turkey..............	8.8	56.2
	9.5	55.8
	10.5	57.6
	12.7	59.4
	13.9	63.3
	15.7	63.9
	16.7	65.1
Tenmarq............	9.8	60.2
	10.7	59.5
	11.2	58.5
	12.3	59.1
	13.7	61.0
	15.3	63.1
Cheyenne...........	10.1	56.0
	10.9	56.4
	12.1	57.6
	13.9	59.4
	15.3	60.7
	16.2	62.1
Michigan Wonder.....	10.1	55.9
	10.8	56.7
	12.3	57.3
	13.5	60.4
	15.0	59.3

Turkey, Tenmarq and Cheyenne are hard red winter wheats, while Michigan Wonder is a soft winter wheat. The figures show that the absorptions increase with the larger protein contents, but not to the same extent in the different varieties. This indicates that the best absorption for the flour of one variety may not be the best for the flour of another variety even if protein contents are the same. The figures also show that

the rate of change in relation to protein content is not as great with the low protein flours as with the high, indicating that the relationship is curvilinear.   Some workers find that below 9 percent protein there is little or no further decrease in absorption.   This is due to the increasingly larger relative proportion of water absorbed by the starch as the protein content decreases.

FLOUR STORAGE

Freshly milled flours are found to give variable baking results, generally yielding bread of unsatisfactory quality.   Clark (*188*) maintains that every flour, if it is not properly stored, will fail to attain its optimum performance when put into production.   The critical factor in storage appears to be flour respiration during which certain biological changes take place which mature and age the flour.   This phenomenon is also called sweating since one of its by-products is moisture.   According to Clark, if bread is to be produced from a mildly sweating flour, the best procedure is to reduce absorption by 2 to 5 percent, reduce the yeast food, set the sponge at a cool temperature, reduce the fermentation time of both the sponge and the dough, add yeast at the dough stage, bring the doughs out at a cool temperature, reduce the steam in the proof box and in the oven and reduce the proof time.   Even then the bread will generally lack volume and exhibit a foxy red crust color, a harsh texture, an open grain and an acid taste and odor.   The bread will be definitely inferior, and will stale rapidly.

Since the keeping quality of flour during prolonged storage is largely determined by its moisture content, the effects of varying atmospheric influences upon the changes in moisture content and net weight of flour have been the subject of numerous studies.   It has been clearly established that flour possesses hygroscopic properties which cause its moisture content to fluctuate with changes in the relative humidity of the surrounding atmosphere.   The rate of change in moisture content is usually more rapid in smaller packages of flour than in larger ones.   As a rule flour will lose in weight when stored in an atmosphere having a relative humidity below 60 percent.   Flour which has been exposed to a dry atmosphere will slowly reabsorb some of the lost moisture but will not recover all of the moisture lost.   Fairbrother (*189*), for example, has found that a flour sample failed to recover in 17 days of storage at a relative humidity of 75 percent the weight it lost overnight at 40 percent relative humidity.   Anker, Geddes and Bailey (*190*) conclude from extensive experiments that the partial drying of flours even at atmospheric temperatures apparently reduces permanently their hydration capacity.

Fisher, Halton and Carter (*191*) have carried out extensive investiga-

tions of the changes which occur in flour during storage of 18 months' duration. They confirmed the previous observation that all flours improve in baking quality during storage up to a point, beyond which deterioration sets in which continues until the flour is entirely unfit for bread-making. Depending upon the wheat variety, and given normal storage conditions, storage may extend over several years with progressive improvement of baking quality, or it may not safely exceed a few months. The reactions occurring during flour storage appear to be quite complex. Thus these workers have found that after the first deterioration has proceeded for some time, a second improvement sets in, which in turn is followed by a second deterioration. They also found a similar periodicity to occur in many of the chemical properties of the flour, such as hydrogen ion concentration, buffer value, total acidity, soluble nitrogen and, above all, in amount and quality of the washed out gluten. These changes vary in rate of rapidity and degree with different grades of flour and with different moisture contents, being more marked and more rapid the higher the moisture content of the flour. It is suggested that biological activities of molds and bacteria may play an important role in these changes. Storage-deteriorated flour was found to have a marked improving action when added at the rate of 2 percent to otherwise untreated flour, the effect obtained being similar to that resulting from chemical or physical improving treatments.

Halton and Fisher (*192*) also found that considerable absorption of oxygen occurs when flour is stored in air under different conditions. They attribute this oxygen absorption by flour to three main factors: (1) Mites and similar small animals which feed on the flour, breathe in oxygen and breathe out carbon dioxide. This type of animal life can be suppressed by heating the flour to 60° C. (140° F.), or by reducing the moisture content of the flour to below 12 percent, or by treatment of the flour with insecticide. (2) Fungal and bacterial life which exists in flour when the moisture content of the flour exceeds about 12 percent. The microflora of flour causes definite deterioration of flour including oxidation of flour constituents. (3) True chemical autoxidation. This process becomes progressively more rapid as the moisture content of the flour is reduced. This chemical autoxidation of flour consists of oxidation of the fatty constituents of the flour, which results in a reduction in the extractable fat content of the flour and in changes in the chemical nature of the fat, and oxidation of the carotene which brings about a removal of the yellow color of the carotene and hence of the flour. Autoxidation of the fatty constituents was observed only when the flour was stored in oxygen. When flour is stored in air, the oxidation of the flour fat does not apparently occur.

McCaig and McCalle (*193*) followed changes induced by excessive flour aging in the physical properties of gluten, as determined by its hydration between pH 4 and 7. They found that the gluten is deleteriously affected by aging, the effects observed being similar to those produced by the addition of linolic acid. Some of the effects of aging can be removed by extraction of the aged deteriorated flour with ether, although the original quality of the gluten cannot be completely restored. Gluten from aged deteriorated flour swells enormously in 1/10 *N* acetic acid. This hydration is not an indication of good quality but rather of resistance to dispersion. Some freshly milled flours produce glutens which possess the physical characteristics of gluten from excessively aged flour. These authors interpret their observations as indicating that the quality of gluten depends to a considerable extent on the nature of the adsorbed lipoids. Many of the characteristics of gluten are determined by relatively insoluble, as yet unidentified lipoid substances. When these lipoids are absent, or when fatty acids are formed during aging, the gluten quality is deleteriously affected.

Jones and Gersdorff (*194*) studied the effect of storage under different conditions upon the proteins of white flour, whole wheat flour, and wheat kernels at various intervals over a period of two years. They found three types of alterations to occur upon storage: (1) There is a decrease in the solubility of proteins; (2) there is a partial breakdown of the proteins as revealed by a decrease in true protein content and an increase in amino nitrogen; and (3) a decrease in protein digestibility. The extent of the observed changes was governed by the storage temperature, type of container, duration of storage and the form in which the material was stored. Storage at room temperature and in air-permeable containers such as bags resulted in greater changes than when the samples were stored at freezing temperatures and in sealed glass jars. Changes in white flour were generally greater than in whole wheat flour. The greatest decrease was found in solubility in the proteins of white flour in 3 percent sodium chloride solution. When stored in a bag at 76° F. for two years, the percentage decrease amounted to 61 percent. The authors ascribe the alteration of the proteins to the effect of enzymes and oxidation.

From the standpoint of the practical baker, many difficulties encountered with flours are due to inadequate aging rather than to an inherent lack of baking quality. Flours stored at low temperatures, such as prevail in unheated storage rooms during winter months, will not perform properly, even though storage may have been extended over several weeks. The explanation lies in the greatly reduced enzymatic action at low temperatures. Many such flours will be found to perform satisfac-

torily if they are transferred to a heated storage room a day or two prior to their use. This pre-warming of flour cannot be circumvented by the use of warm doughs, as is frequently attempted in practice. Even in instances where flour is aged at the mill, it is highly desirable to hold the flour at the bakery for a minimum period of a week to permit an equalization of its temperature.

The storage room at the bakery should be a light, dry, well aerated room maintained at a temperature of 75° to 80° F. Normal flour will require approximately three to four weeks of storage to pass through its sweating period and to attain a temperature throughout its bulk of approximately 70° F.

WHEAT GERM FLOUR

Finely ground wheat germ, when added in its raw state to dough in excess of 3 percent, affects both the dough and the bread. It is now generally accepted that the deleterious effect results in the main from the glutathione present in the germ which acts on the gluten, thereby weakening the dough and rendering it sticky and difficult to machine. The bread will have a more open grain and a poorer volume. When more than 5 percent of germ is added, normal bread can no longer be produced. Even when smaller increments of germ are added, it is well to use a strong flour with good fermentation tolerance and a relatively high protein content since germ will tend to soften any dough.

Several investigators have concerned themselves with the problem of identifying the particular constituents that are responsible for the degrading effect produced by the germ on the baking quality of flour. Sullivan and Near (*195*) attributed the poor quality of the gluten from the whole wheat as compared with that from patent flour to a higher lipoid content. This view was supported by Johnson (*196*) who suggested that flour might be improved by extraction with ether. He found that in every case the bread produced from ether-extracted flour was superior to that from the corresponding natural flour, the greatest improvement being found in flours richest in lipoids. On the other hand Martin and Whitcomb (*197*) noted that only in some cases was there an improvement in the loaves of ether-extracted flours, other flours after extraction giving inferior results. Bull (*198*) also failed to observe an improvement in baking quality on extraction of the lipoids of germ with ether, when compared with pure germ, and concluded that the deleterious effect of germ was not attributable to its lipoid content. To further underline this point, this investigator incorporated up to 8 percent of germ oil into a loaf without producing a marked difference in the loaf. Further extraction studies revealed that the harmful substances were insoluble also

in alcohol, but soluble in water. The general conclusion reached by Bull was that the degrading effect is partly due to (1) the proportion of minerals present, in particular the amount of magnesium oxide in relation to calcium oxide, and (2) the presence of the non-protein compound asparagine.

The deleterious effects of germ may be reduced in various ways. These have been summarized by Sullivan (*199*). Setting of long time germ sponges with 0.3 to 0.5 percent yeast food will prove beneficial. Milk has been found to lessen the damaging effect of germ. This is attributed to the dehydrase enzymes of milk which are capable of oxidizing the sulfhydryl group of glutathione and thereby function in a manner similar to that of bromate and other oxidizing agents of certain yeast foods. Preparing a pre-ferment of germ, yeast and water will also reduce the harmful effects of the germ. Hullet (*200*) has investigated this last method and has found it to be highly effective. According to this investigator, if a ferment consisting of germ, yeast and water is allowed to stand for several hours, during which time fermentation takes place, the reduced glutathione disappears. The time needed for the disappearance depends on temperature and yeast volume, increase in either hastening the process. The ferment is then mixed with additional flour, salt, sugar and more water and made into a dough from which bread is made in the usual manner. Up to 4 percent of germ (on the flour basis) may be used in white bread without encountering the typical defects usually associated with the use of untreated germ. An important fact is that a yeast quantity which ripens ordinary dough in eight hours will, after treatment in the ferment, attain the same maturation in only two hours. Since no flour is present in the ferment, no direct dough ripening is possible and it must be assumed that some chemical process occurs in the ferment which is equivalent to a pre-maturation of the dough. The method has theoretical significance by indicating that glutathione elimination apparently plays an important part in the ordinary dough ripening process.

PREPARED FLOUR MIXES

So-called prepared flour mixes are products in which all dry ingredients, such as flour, sugar, dry milk solids, egg powder, shortening and, in some instances, yeast are blended according to definite formulas directly at the manufacturers' plant. Flour mixes were introduced some thirty years ago and have within the past few years undergone considerable development with respect to both variety and quality. In processing such dry mixes, the baker adds the proper amount of liquid, mixes the dough or batter, and then continues in the conventional manner. The principal advantage of the use of dry mixes is convenience since they

obviate the need for separate scaling of each of the various ingredients. Other advantages include reduced labor cost, lessened inventory and storage requirements, and uniformity of baked products, to mention only the more important.

Prepared mixes used currently in commercial baking may be classified into three general groups. The first of these includes the prepared cake doughnut mixes leavened by baking powder only. For these mixes unbleached, naturally aged soft wheat flour is used (*201*). The additional ingredients include sugar of controlled particle size, moisture and purity; shortening possessing adequate stability; spray-dried nonfat milk solids; a leavening agent; and dried yolk. Some doughnut mixes also contain small percentages of soy flour and cottonseed flour. Prepared doughnut mixes are available in a large variety of types, including specially formulated mixes for hand-cut doughnuts, machine-cut doughnuts, round, stick and ball shaped doughnuts, and old-fashioned doughnuts.

The second group of prepared mixes includes the prepared yeast-raised mixes for sweet goods. These are the outgrowth of the period of sugar and fat shortages which made it difficult for bakers to operate normally toward the end of World War II. There are several types of yeast-raised mixes. The first is a sweet dough mix which yields a basic sweet dough for the production of a variety of goods, such as coffee cake, sweet rolls, yeast-raised doughnuts, and others. It has the disadvantage of all basic sweet doughs in that it is a compromise dough designed to yield a variety of acceptable, but not optimum quality sweet goods. This is quite understandable because the requirements of, for example, a coffee cake differ from those of a yeast-raised doughnut and a dough making excellent coffee cake will produce less acceptable doughnuts. This has led to the development of additional special mixes for various types of sweet goods. Principal of these is the coffee cake mix, which can be used for either straight or sponge doughs. This special coffee cake mix possesses good fermentation tolerance, machines well, and is suitable for the retarded dough process. It may be used for Danish pastry and has the additional advantage of flexibility since it can be either enriched by the addition of eggs or made leaner by the addition of plain flour. Yeast-raised sweet dough mixes contain either an unbleached hard wheat patent flour exclusively, or a blend of hard flour with soft wheat flour. Most prepared yeast-raised mixes contain high emulsifying type shortenings which are characterized by excellent stability, emulsification and moisture dispersing qualities.

The third and at the present time least important group of prepared mixes includes a variety of prepared cake mixes, such as white, yellow, spice and devil's food mixes. These cake mixes require the largest num-

ber of individual ingredients, such as flavors, eggs, shortenings, cocoa, chemical leaveners, etc., which must be accurately blended for optimum results. It is in these types of mixes that the factor of convenience for the baker using such mixes becomes most apparent. The number of cake varieties for which prepared mixes are being developed is constantly increasing so that all conceivable needs of commercial bakers are being rapidly met.

CHAPTER IX

MISCELLANEOUS FLOURS

RYE FLOUR

Whereas rye is a relatively unimportant bread cereal in the United States, it occupies a leading position in several European countries, including Germany, Poland, Scandinavia and Russia, where rye bread constitutes a staple food item. In 1939, the world rye crop amounted to slightly over 2 billion bushels, or about one-third that of wheat. Of this amount, approximately 65 percent was produced in Germany and Russia alone, and only about 2.5 percent in the United States.

Rye is grown principally in colder regions where it will thrive under climatic and soil conditions which are unsuitable for wheat cultivation. With increasing availability of export wheat, the consumption of rye as a bread cereal has declined markedly during the past several decades even in countries where it formerly constituted a nearly exclusive bread cereal. The principal reason for this decline is the greater palatability of wheat bread. Present-day rye breads in nearly all countries usually contain liberal admixtures of wheat flour to improve the general characteristics of the final product. From a nutritional viewpoint there is no practical difference between rye flour and wheat flour. French and Mattill (202), for example, have shown that the biological value of the proteins of white and rye breads are of the same general order. Schulerud (203) has stated that, depending upon the degree of extraction of the flour used, wheat bread has a digestibility of 80 to 98 percent, while that of rye bread is 78 to 95 percent, a difference which is hardly significant.

COMPOSITION OF RYE AND ITS MILLED PRODUCTS

The average chemical composition of the rye cereal is shown in the following table adapted from data compiled by Morrison (204). It will be noted that the magnitude of the various constituents differs but little from the ranges encountered in wheats. However, there are some significant differences between wheat and rye in the composition of the individual components.

Rye Proteins. The protein of rye consists principally of a prolamin (gliadin) and a glutelin, with smaller quantities of an albumin (leucosin)

TABLE 60.   AVERAGE COMPOSITION OF RYE

	Percent
Protein	12.3
Fat	1.7
Fiber	2.3
N-free extract	71.7
Ash	2.0
Moisture	10.0

and a globulin (edestin) (*205*).   Kent-Jones and Amos (*153*) give the following quantitative composition of rye protein:

Gliadin	42%
Glutelin	42%
Globulin	8%
Albumin	8%

Although the analysis of rye albumin and wheat albumin is identical, the rye albumin coagulates at a slightly higher temperature than does wheat albumin.   There also exists a slight difference in the elementary analysis of the globulins as obtained from wheat and rye.   The gliadin of rye appears to be identical to the gliadin of wheat.   The glutelin of rye, however, differs markedly from the glutenin of wheat flour.   This is the reason for the fact that it is impossible to wash gluten from a rye flour dough as can be readily done with a wheat flour dough.   The inability of

TABLE 61.   AMINO ACID COMPOSITION OF RYE PROTEINS

Amino Acid	Gliadin	Glutelin
	Percent	Percent
Glycine	0.1	—
Alanine	1.3	—
Valine	—	—
Leucine	6.3	—
Isoleucine	—	—
Proline	9.8	—
Phenylalanine	2.7	—
Tryosine	1.2	—
Serine	0.1	—
Threonine	—	—
Methionine	1.5	—
Aspartic acid	0.3	—
Glutamic acid	33.8	—
Arginine	2.2	7.1
Histidine	0.4	2.7
Lysine	0.4	5.4
Tryptophane	0.7	—
Cystine	2.6	2.6

rye flours to give rise to a definite gluten structure during dough mixing accounts for the small compact loaves which result from pure rye flour, and for the volume depressing effect that is obtained when a large admixture of rye flour is made to wheat flour.

The amino acid composition of rye proteins is given in Table 61 which is condensed from data compiled by Jones [cited by W. F. Geddes (*136*)].

Minerals of Rye. The average content of the principal mineral constituents in rye is given in the following table, based on data compiled by Beeson (*206*).

TABLE 62. AVERAGE PERCENTAGES OF
MINERAL ELEMENTS IN RYE

	Percent
Calcium	0.115
Magnesium	0.14
Potassium	0.53
Sodium	0.04
Phosphorus	0.37
Chlorine	0.02
Sulfur	0.18
Iron	0.0065

It will be noted that potassium and phosphorus are present in highest amounts. Nearly all of the phosphorus occurs in organically bound form, with about one-half forming part of phytin. This substance, which is nutritionally significant because it interferes with the proper absorption in the human body of dietary calcium and iron, is a magnesium or calcium salt of phytic acid which consists of one molecule of inositol combined with six molecules of phosphoric acid. The phytin occurs principally in the outer portions of the grain, especially in the aleurone and bran layers. Part of the phytin is eventually hydrolyzed by the enzyme phytase during fermentation and the early stages of baking into phosphoric acid and inositol, a hexahydric alcohol. The presence of phytin has been demonstrated also in wheat and its milled products, in which its distribution is the same as in rye. The nutritional inferiority of low grade flours is in part attributable to their relatively high phytin content which results in an improper dietary mineral balance when bread made from such flours constitutes an important part of the daily diet. The enrichment of such flours with calcium corrects this particular deficiency.

Carbohydrates of Rye. The carbohydrates which occur in rye flour, although they are of the same general type as those of wheat flour, differ in several respects from the latter. As in wheat, they include starch, fiber, pentosans and hemicelluloses, dextrins and sugars. Of primary

interest are the pectin-like carbohydrate gums, thought by some to consist principally of pentosans, which occur in much higher percentages in rye than in wheat flours and which appear to be responsible for the well-known stickiness of rye doughs. There is also some evidence that they may exert an effect upon the rye proteins in such a manner as to prevent gluten formation. Thus Schulerud (*203*) cites the work of Fellenberg who found that when 2 percent of rye gums are added to wheat flour, gluten can no longer be washed from the flour so treated. This effect is explained on the basis of the high swelling capacity of these gum substances which thereby withdraw water from the gluten and prevent its proper swelling. The gluten particles are thought to be surrounded by the hydrated gums so that they cannot adhere together. Geddes (*136*) also points to the possibility of these gums interfering with the formation of the gluten complex in mixtures of rye and wheat flours. He states that if 35 percent of rye flour is added to wheat flour, slightly more gluten can be washed from the mixture than from an equivalent quantity of wheat flour alone. When, however, increasing amounts of rye flour are added, there is a reduction in the gluten obtained and when the mixture contains 50 percent rye flour, no gluten at all can be obtained. The inferior baking properties of rye flour are attributed to this gum which is dispersed under the action of such organic acids as lactic and acetic. This may explain the superior quality of rye bread obtained by sour-dough fermentation as compared with yeast fermentation. It has thus far proved impossible to isolate the gums from rye bread, indicating that they are in some manner eliminated during fermentation.

Rye flour, in general, contains somewhat higher contents of soluble sugars and dextrins than does wheat flour. Also, the sugar-yielding substances appear to be more susceptible to enzymatic hydrolysis so that rye flours as a rule possess considerable fermentation capacity. Rye flour contains several times the amount of a nonreducing trisaccharide sugar, trifructosan, as does wheat flour. Schulerud (*203*) has determined the trifructosan content of rye flour to average 2 percent, and that of wheat flour 0.4-0.5 percent. This difference serves as a basis for a chemical test developed by Tillmans (*207*) for determining the amount of rye flour admixtures with wheat flour.

Although apparently no chemical differences exist between wheat and rye starches, the latter show some distinguishing characteristics in their physical behavior which differentiate them from wheat starches. For example, whereas some 90 percent of rye starch is gelatinized at a temperature of 65° C. (167° F.), only some 50 percent of wheat starch is gelatinized under the same conditions (*203*). Also in contrast to wheat starch, the reaction of rye starch during gelatinization is considerably

influenced by the age of the rye flour. Schulerud has shown that in a freshly milled flour the starch is readily gelatinized, permitting the alpha-amylase of the flour to degrade the starch rapidly. This is of considerable practical significance in baking since when this starch degradation proceeds too far the resultant bread will have a moist doughy crumb. The excessively degraded starch is unable to absorb the water liberated by the coagulated protein during baking.

With increasing age of the flour the starch gains in resistance toward gelatinization, leading to higher gelatinization temperatures. This is accompanied by a corresponding decline in the liquefying action of the diastase. The correct relationship between the rate of gelatinization and the rate of diastatic activity is of primary importance for the ultimate character of the bread. A quality rye flour is one in which these two factors are in proper balance. It is essential that some starch degradation take place to impart the necessary pliability to the crumb and thereby prevent the tearing of the dough during oven spring. A common bread fault encountered when old rye flours are used is, in fact, the tendency of the loaf to show breaks at the sides or in the bottom crust. This change in gelatinization resistance of rye starch is viewed as a kind of hardening of the starch granules after they have been exposed to the atmosphere by the milling process. It does not occur in the whole grain even when stored for prolonged periods.

Rye Fats. The fat content of rye has been variously recorded to be within the range of 1.7 to 2.3 percent, and that of rye flour, 0.65 to 1.25 percent, depending, in the latter case, upon the degree of flour extraction. In the whole grain, the fat is concentrated primarily in the germ portion, of which it constitutes about 12 percent of total matter. Ether-extracted rye fat is a yellowish brown oil consisting principally of the glycerides of oleic and palmitic acids. Rye also contains approximately 0.5 percent of phospholipoids or lecithins. The fat content of rye flour is of practical importance for the storage stability of the flour. It has been indicated above that rye flours tend to harden upon storage. This hardening or aging effect is partly attributable to the enzymatic cleavage of the flour fat by lipases, resulting in the formation of free fatty acids. Schulerud (203) has shown that free fatty acids bring about a change in both the protein and starch behavior by inhibiting the swelling capacity of the protein on the one hand, and the gelatinization of the starch, on the other. Hence, the storage stability of rye flour is largely determined by its fat content which, in turn, is influenced by the degree of milling extraction, with low grade flours containing higher fat contents. The higher the fat content, the shorter the storage life of the flour, if excessive aging phenomena are to be avoided.

Rye Milling. The rye milling process differs in several respects from that of wheat milling, being in general simpler than the latter. As with wheat, the rye grain is subjected to an initial cleaning and screening. The moisture content of the grain is of considerable importance from a milling standpoint, since if the grain is too dry, the bran becomes very brittle and is reduced into particles too small to be effectively removed from the flour, whereas if the grain is too moist, there is a tendency of the rye endosperm to gum up the rolls. European experience indicates that a moisture content of 14 to 16 percent is most suitable. The grain is passed through a number of break rolls, followed in each instance by a removal of the liberated flour by means of sifting and final passage through reduction rolls. Since rye does not yield middlings, there is little or no purification of the milling stocks. The final streams therefore contain considerable offal.

Rye flour types are generally classified into white, medium and dark flours. The first type aims at as light a color as possible and corresponds most closely to the patent flour of wheat. Its ash content is generally within the range of 0.55 to 0.65 percent, and its protein content may vary from 6 to 9 percent. It is the only type of rye flour that is ever chemically bleached. According to Kirk (*208*) up to 40 percent of good white rye flour can be added to a standard clear wheat flour without diminishing the loaf volume appreciably. Medium rye flour, which corresponds most nearly to an 80 percent extraction wheat flour, is much darker in color than the white rye flour, containing a fair proportion of bran particles. Its ash content will range from 0.65 to approximately 1 percent, and its protein content is considerably higher than that of the lighter flour. There is also considerable variation in its color since millers will so conduct their operations as to produce the color desired by the trade. Medium rye flours in admixtures up to 30 percent to a good standard clear wheat flour should not depress the loaf volume markedly. Dark rye flour represents the low grade product containing much of the bran and having a dark color. Its ash content ranges from 1 to 2 percent and its protein from 12 to 16 percent. Addition of up to 20 percent of dark rye flour to a standard clear flour should not depress the loaf volume appreciably.

MALTED WHEAT FLOUR

Diastatic supplements, generally in the form of malt cereal flours or syrups, have long been used by bakers to supplement bread flours. Millers as a rule correct diastatic deficiencies of flour by the suitable addition of malted flours, preferably ground from wheat which has been subjected to the proper degree of germination. On the other hand, bakers who have ac-

cess to adequate laboratory facilities frequently prefer to carry out diastatic supplementation directly in the baking plant.

Freeman and Ford (*209*) have summed up the reasons for the use of malt supplementation to be principally (1) to increase gas production, (2) to improve the crust color, (3) to increase the moisture of the crumb, and (4) to impart additional flavor. Bakers observed early, however, that when an excess of malt products was used, the dough tended to become too soft and sticky upon fermentation for satisfactory handling and machining. Various explanations have been advanced to account for this softening of the dough. Some investigators, noticing the increase in proteolytic activity which results from the germination of cereals, inclined toward the view that the proteolytic enzymes of the malt product degraded the gluten structure of the dough, thereby bringing about a far-reaching liquefaction. Moundfield (*210*), for example, had found in extensive studies of the proteolytic activity of malted wheat flours that the proteinases of this cereal increased about six-fold when germination was carried on for four days, and about ten-fold when germination was extended over seven days, when the proteolytic activity was measured by the use of the protein edestin as a substrate. On the other hand, he also observed that the degree of hydrolysis obtained was far less when gluten or a mixture of glutenin and gliadin were used as the substrate. At the same time, data were accumulated which tended to show, first, that the amount of proteolytic enzymes added to dough through the medium of malted wheat flour was insufficient to produce the far-reaching softening of the dough, and second, that the same extent of softening resulted when malted flour extracts, in which the proteolytic enzymes were inactivated, were added to fermenting doughs (*211*). Evidently some other factor or factors present in malted wheat flour are responsible for the increased dough mobility which results from excessive use of malted products.

Baker and Hulton (*212*) appear to have been the first to postulate that the beneficial effect of malt supplement was due to the action of the starch liquefying enzyme provided by this means. It was observed early that the Lintner value, which reveals the saccharogenic activity resulting from the combined actions of alpha- and beta-amylases, but which is determined largely by the content of the beta-amylase, gave only poor correlation with increases in loaf volume or gas production. In 1933 Kosmin (*213*) attributed the development of sticky doughs to the starch dextrinizing and liquefying alpha-amylase present in malt wheat flour. This enzyme is practically absent in normal, ungerminated flour, being either produced or activated during the germination of the whole grain. The characteristic amylase of normal flour is beta-amylase which hydrolyzes starch into

maltose sugar. However, this enzyme is able to attack only injured starch granules. Alpha-amylase, on the other hand, splits up starch into dextrins, bringing about a pronounced liquefaction of the substrate. Blish, Sandstedt and Mecham (*214*) have further postulated a "raw starch factor" in malted wheat flour which is very similar in its activity to alpha-amylase and which is able to attack raw starch.

Subsequent studies by numerous investigators, including among others Munz and Bailey (*215*), Sandstedt (*216*), Sandstedt, Jolitz and Blish (*217*) and Freeman and Ford (*209*) have shown the alpha component of malt amylase to be responsible for increased loaf volume. The relationship of alpha-amylase activity to the gassing power of sugar-deficient doughs is explained by Kneen and Sandstedt (*218*) on the basis that the abundance of beta-amylase already present in the flour can saccharify only 60 percent of the "available" starch of that flour. Alpha-amylase, in combination with the beta component, can carry hydrolysis far beyond that point. In addition, alpha-amylase seemingly is the component of malt responsible for the hydrolysis of "raw" undamaged wheat starch. The same authors point out that the function of alpha-amylase does not stop with merely providing sufficient sugar for fermentation, for in doughs in which the sugar content has been so adjusted as not to constitute a limiting factor, there was still an improvement in loaf volume when malt was added. Alpha-amylase thus apparently acts to increase the gas retention capacity of doughs by the production and modification of dextrins.

One important practical conclusion to be drawn from all these data is that malt should be purchased on the basis of its alpha-amylase activity since it is the alpha component which represents the significant factor in malt supplementation. A malt having a high Lintner value does not necessarily have a high alpha-amylase activity, since the Lintner method measures both alpha- and beta-amylases and does not distinguish between these two components.

SOYBEAN FLOUR

The soybean, or soya bean, is one of the oldest agricultural crops cultivated by man. In China, where it forms the most important source of food protein, its origin is lost in antiquity. From there, the soybean has spread over a large portion of the world, being now extensively grown in the United States and Europe, as well as the Far Eastern countries. Whereas this legume is largely grown as a food crop in the Orient, its principal uses in other parts of the world are for the production of oil and meal. More recently, the increased production of soybeans in the United States has led to the development of numerous food, feed, and industrial uses for both the meal and the oil.

Chemical Composition. The soybean seed consists principally of protein, oil, carbohydrates, and mineral constituents. The proportions in which these various component materials are present are influenced considerably by soil, climatic conditions, and variety. The variation in composition, as revealed by analyses of hundreds of samples, have been summarized by Bailey, Capen and LeClerc (*219*) and are given in Table 63.

TABLE 63.   CHEMICAL COMPOSITION OF SOYBEANS

	Minimum	Maximum	Average
	%	%	%
Moisture............................	5.02	9.42	8.0
Ash................................	3.30	6.35	4.6
Fat................................	13.50	24.20	18.0
Fiber..............................	2.84	6.27	3.5
Protein............................	29.60	50.30	40.0
Pentosan...........................	3.77	5.45	4.4
Sugars.............................	5.65	9.46	7.0
Starch-like substances by diastase......	4.65	8.97	5.6
P_2O_5............................	1.50	2.18	1.7
K_2O.............................	2.01	2.64	2.3
CaO...............................	0.49	0.63	0.5
MgO...............................	0.46	0.55	0.5
Weight per 1,000 seeds, grams.........	40	248	150

It will be noted that the fat content ranges from a low of 13.5 percent to a high of 24.2 percent, while the protein content varies from 29.6 percent to more than 50 percent. Correspondingly large variations occur also in the other constituents.

The composition of soybean flours is also subject to variations, depending to a considerable extent upon the type of processing employed and the composition of the original bean. So-called full fat flours, which are processed from the bean without extensive preliminary treatment except for the removal of the hull, tend to show greater variability of composition than do so-called expeller pressed and solvent extracted low fat flours. The range in values encountered in commercial flours has been recorded by Bailey, Capen and LeClerc in 1935 (*219*) and is shown in Table 64.

More recently, Bohn and Favor (*220*) obtained the typical analyses of commercially available soybean flours shown in Table 65.

Protein. These analyses show that soya flour is exceptionally rich in protein, the principal component of which is glycinin, a globulin which contains all the amino acids essential for growth. Glycinin constitutes approximately 80 to 90 percent of the total crude protein, the remainder being made up of albumin and glutelin. It is thus seen that soya protein differs considerably from wheat protein in its chemical composition. The

TABLE 64. COMPOSITION OF HIGH FAT, PRESS CAKE, AND SOLVENT-EXTRACTED SOY-
BEAN FLOURS

	High fat flours (17 samples)			Press cake flours (14 samples)			Solvent-extracted flour (1 sample)
	Mini-mum	Maxi-mum	Aver-age	Mini-mum	Maxi-mum	Aver-age	
	%	%	%	%	%	%	%
Moisture...................	4.09	10.41	7.04	5.60	9.22	7.70	7.73
Ash........................	3.68	5.18	4.60	5.46	6.03	5.75	2.66
Fat........................	17.61	23.93	21.11	6.18	8.88	7.30	1.58
Fiber......................	1.50	4.33	2.30	1.96	5.87	3.03	3.04
Protein....................	34.44	49.37	41.55	43.81	49.76	47.45	68.74
5% K_2SO_4 soluble N (% of total N)............	6.80	50.50	25.20	17.00	56.40	35.00	8.90
1% NaCl soluble N (% of total N)............	6.40	36.20	21.60	12.20	37.20	26.50	7.00
70% alcohol soluble N (% of total N)............	1.70	9.50	3.34	2.10	3.80	2.80	2.40
Reducing sugar before inver-sion.....................	0.00	2.37	0.52	0.00	1.04	0.45	0.03
Reducing sugar after inversion.	5.37	11.06	9.29	10.56	12.44	11.44	0.06
CaO.......................	0.21	0.36	0.28	0.28	0.56	0.35	0.61
P_2O_5......................	0.93	1.47	1.21	1.29	1.56	1.40	1.03
Lecithin...................	0.17	1.62	1.10	0.76	1.77	1.30	0.66
Alkalinity[1]................	18.00	29.40	24.10	27.90	34.10	30.20	8.80
Urease activity[2]............	0.20	6.00	2.50	0.20	5.20	2.40	0.90

[1] Cc. of N acid per 100 g. sample
[2] Cc. N/10 ammonia

amino acid composition of soya protein shown in Table 66 is reported by Block and Bolling (*76*) with the wheat gluten composition being included for comparison.

Hafner (*221*), in discussing the nutritional value of soya flour, points out that it is especially its high lysine content as compared with gluten protein that renders the former a valuable enriching adjunct to wheat

TABLE 65. TYPICAL ANALYSIS OF SOYBEAN FLOURS

Type	Moisture	Ash	Fat	Protein N × 6.25	Crude fiber	Nitrogen-free extract
	%	%	%	%	%	%
Full fat................	5.0	4.75	23.5	41.5	2.3	23.0
Expeller pressed........	5.0	5.50	7.5	50.0	3.0	39.0
Solvent extracted.......	8.0	5.75	1.8	52.0	3.0	32.4

TABLE 66. COMPARATIVE AMINO ACID COMPOSITION OF SOYA
PROTEIN AND WHEAT GLUTEN PROTEIN

	Wheat gluten	Soybean
Arginine........................	3.9	5.8
Histidine.......................	2.2	2.3
Lysine.........................	1.9	5.4
Tyrosine.......................	3.8	4.3
Tryptophane....................	0.8	1.5
Phenylalanine...................	5.5	5.4
Cystine........................	1.9	1
Methionine.....................	3	2.0
Threonine......................	2.7	4.0
Leucine........................	12.0-2.6	6-8
Isoleucine......................	3.7-0.2	4
Valine.........................	3.4-0.5	4-5
Sulfur.........................	1.1	1.1

flour. The excellent nutritive value of soya flour is apparent from the
following data obtained by this author.

TABLE 67. NUTRITIVE VALUE OF PROTEIN IN SOY FLOUR AND WHEAT
FLOUR

Sole Source of Dietary Protein	Grams gain per gram protein eaten[1]	Relative Protein Efficiency (%)
Extracted soy flour (low fat)............	1.83	100.0[2]
Full fat soy flour.....................	1.70	92.9
Raw soybeans........................	0.98	53.5
Patent wheat flour[3]....................	0.71	38.8
Patent wheat flour, enriched[3]............	0.66	36.1
Whole wheat flour....................	1.14	62.3

[1] Nutritive value
[2] Arbitrarily assigned a relative protein efficiency of 100% on basis of its nutritive
value of 1.83 g. gain per gram protein eaten.
[3] All three wheat flours were milled from hard spring wheat of similar analysis and
origin. The patent flours were commercial runs; the whole wheat was produced by grinding
whole wheat in a laboratory mill.

In later nutritional tests, Carlson, Hafner and Hayward (*223*) report
upon results obtained with three biological methods used to evaluate the
nutritional value of white bread containing varying amounts of soy flour
and nonfat dry milk solids, respectively, and of whole wheat bread. The
methods used measured the nitrogen balance, growth, and body protein
storage of laboratory animals. The data obtained by the three methods
indicated that the nutritional quality of the white breads containing 3
percent soy flour and 3 percent milk, respectively, was equal and sig-
nificantly better than of white water bread. When 5 percent white soy
bread was compared with 6 percent white milk bread, they were found

to be practically equal, and both were either equal or slightly superior to the whole wheat water bread. The nutritional improvement of bread proteins by the addition of either soy flour or nonfat dry milk is due primarily to the comparatively high lysine and valine contents of these additives. Thus the lysine content of soy protein, as given by these authors, is 5.4 percent and that of milk protein, 7.5 percent; the valine content of both proteins is 4.5 percent.

The protein of soya flour differs further from wheat gluten in that it lacks elasticity. On the other hand, it exhibits a strong "binding power." This binding power, according to Hafner (*222*) provides some resistance to dough expansion, the effect being somewhat proportional to the level of soya flour employed. It can be partially overcome by adjustment of the quantity of water used in the dough and by prolongation of proofing time. The binding power of solvent-extracted soya flour is closely related to its high water absorption. Bohn and Favor (*220*) determined the water absorption of soya flours by means of a farinograph and found that, at 500 Brabender units consistency, full-fat soya flour has an absorption of 85 percent, whereas the solvent-extracted flour has an absorption of 110 percent. These authors conclude that for all practical purposes, the solvent-extracted soya flour will absorb an amount of water equal to its weight when mixed with wheat flour to dough consistency. In the case of full-fat flour, no significant effect upon dough absorption results from normal additions of the soya product.

Finney (*224*) investigated the baking properties of three samples of low-fat soy flour, two of which were extracted with hexane, while the third was extracted with alcohol. He found that excellent bread can be made with soy flour additions up to 8 percent provided the quantity of potassium bromate used in the formula is increased according to the amount of soy flour used. Loaves containing soy flour and properly adjusted increments of oxidizing agent were superior to bread baked from wheat flour alone as measured by loaf volume and fineness of grain. The amount of bromate required for optimum loaf volume increased, in general, with the concentration of soy flour. Thus, 5 mg. per 100 g. of wheat flour were required for 8 percent of soy flour, compared with only 1 mg. for wheat flour alone. Both the absorption and the mixing time increased with the amount of soy flour used. The change in crumb color produced by adding as much as 4 percent of soy flour probably would not be noticed by most consumers, according to this author.

Bayfield and Swanson (*225*) reported similar observations. They found that for optimum volume, bread containing 1.5 percent of low-fat soy flour requires about 2 mg. more potassium bromate per 100 g. flour than nonsoy bread. Greater additions of soy flour required additional

increments of bromate. Loaf volume was also found to be increased with shorter fermentation times, if yeast and bromate were increased to the optimum. With optimum yeast, bromate, and fermentation time, these authors found that bread containing up to 6 percent of soy flour was approximately equal in volume to the nonsoy control bread. For optimum texture, extra bromate and shorter fermentation were required where soy flour was used. There was a significant reduction in fermentation and baking loss in doughs containing soy flour. Crumb color was insignificantly affected with 3 percent soy flour and optimum conditions. With 6 percent soy flour and optimum conditions, the crumb color was darker but would probably be considered quite satisfactory for white bread by the consuming public.

Trempel (*226*) has suggested that the use of high-fat soy flour in the making of soft cake will extend the product's shelf life, improve its texture and eating characteristics, and enhance its appearance. Recommended additions range from 5 percent in white cake to 20 percent in chocolate and devil's food cakes, on a flour basis, the following formula adjustments being required: (a) The liquid should be increased by an amount which is equivalent in weight to 125 percent of the soy flour added (i.e., 1 lb. 4 oz. of extra liquid for each pound of high-fat soy flour); (b) the leavening requires a slight upward adjustment on the order of 1 oz. of extra baking powder for every pound of high-fat soy flour; (c) the salt content may also be increased very slightly, about ¼ oz. additional for each pound of soy flour. The soy flour may be incorporated into cake formulas either by sifting or blending with the wheat flour, by suspending in water with thorough agitation in a manner approximating the reconstitution of milk, or by creaming or blending the soy flour with the sweetener, shortening, and eggs. In general, best results are obtained with the two latter methods.

Carbohydrates. The carbohydrates of soybean consist principally of sugars, dextrin, pentosans, galactans, cellulose, and organic acids. Starch is practically absent, or at best present in amounts of less than 3 percent. Street and Bailey (*227*) reported the presence of the following carbohydrates, expressed in percentages of the whole meal: Galactan, 4.86; pentosan, 4.94; sucrose, 3.31; invert sugar, 0.07; raffinose, 1.13; starch, 0.50; dextrin, 3.14; cellulose 3.29; undetermined hemicelluloses, 0.04; total, 21.28. If the organic acids, waxes, color pigments and undetermined carbohydrates are included, a total of 31.08 percent results. Hafner (*221*) reports the following approximate percentages of sugars present in solvent-extracted soya flour: Sucrose, 7-8; stachyose, 5.6-6.6; raffinose, 1.4-2.0; pentosans, 5.6-6.6; galactans, 4.3-6.0; yielding a total of about 26.6 percent of sugars. Stachyose is a tetrasaccharide composed

of one molecule of levulose, one molecule of glucose, and two molecules of galactose, and has the empirical formula $C_{24}H_{42}O_{21}$.

Mineral Constituents. While soybean, as well as soya flour, are relatively rich in mineral constituents, the ash content averaging about 5.5 percent in extracted flour. Soya flour contains considerably more calcium and phosphorus than do any cereal grains, and it constitutes an excellent source of available iron. The mineral content of air-dried soybeans is given in the following table compiled by Markley and Goss (*228*) from various published sources.

TABLE 68. MINERAL CONTENT OF SOYBEANS (AIR-DRY BASIS)

	Percent		Percent
Ash	5.06	Phosphorus	0.59
Potassium	1.91	Sulfur	0.41
Sodium	0.34	Chlorine	0.024
Calcium	0.21	Manganese	0.0028
Iron	0.0074	Zinc	0.0018
Copper	0.0012	Aluminum	0.0007
Magnesium	0.22		

Vitamins. Soya flour is considerably richer in vitamins than patent wheat flour and somewhat richer than enriched white flour. Hafner (*221*) has given the corresponding vitamin values of solvent-extracted soya flour and unenriched white flour shown in Table 69. In interpreting these data,

TABLE 69. VITAMIN CONTENT OF EXTRACTED SOYA FLOUR
AND PATENT WHEAT FLOUR

Factor	Extracted Soya flour (per lb.)	Patent Wheat flour (per pound)
Carotene	340 I.U.	136 I.U.
Thiamine	3.4 mg	0.27 mg
Riboflavin	1.82 mg	0.41 mg
Niacin	27.2 mg	4.5 mg
Pantothenic acid	6.4 mg	2.7 mg
Biotin	331.4 mcg	2.3 mcg
Choline*	1.02 mg	?

* An accessory factor rather than a vitamin
I.U. = International Unit = 0.6 mcg pure beta-carotene
mcg = microgram or 0.000001 g

it should be kept in mind that present enriched white flour contains the following minimum quantities of B complex vitamins per pound: 2.0 mg. of thiamine, 1.2 mg. of riboflavin, and 16 mg. of niacin.

Lecithin and fat. Whole soybean contains normally 13.5 to 24 percent of extractable lipids or fatty material. According to Markley and Goss (*228*), the oil or fat of soybean consists principally of the glycerides

of saturated and unsaturated fatty acids, mixed with several other lipoid materials, including phosphatides, sterols, free fatty acids, etc. Depending upon the method of processing, the soya flour may contain either a low fat content in the range of 0.7 to 7.5 percent, or a high fat content of the order of 23 percent. The lecithin or phospholipoid content varies from 0.5 to 1.5 percent, so that one pound of soya flour contains as much lecithin as 4 to 6 eggs. It represents about 30 to 35 percent of the total phosphatides. Other phosphatides present in soya flour are the cephalins which comprise a group of substances closely related to the lecithins. These soybean phosphatides, which are commercially available under the general designation of vegetable or soybean lecithin, are highly hygroscopic and form colloidal solutions. They owe their great usefulness in food processing to their excellent emulsifying property.

Types of Soya Flour. Commercially available soya flours designed for use by the baking industry are of two general types, namely high-fat or full fat, and low-fat. Low-fat flours, in turn, are differentiated into so-called expeller flours, whose fat content is in the range of 5 to 7 percent, and solvent-extracted flours with a fat content of 1 percent or lower. Full fat flours are produced from cleaned beans treated with steam to remove their unpleasant beany flavor. The beans are then dried, cracked to permit the removal of their hulls, and ground into flour. This steam treatment, of which several variations have been developed, not only improves the flavor of the product but greatly increases its stability, so that the flour can be stored for prolonged periods without rancidity development despite its high fat content. In the expeller process the preliminary treatment of the beans is essentially the same. The grist which results from passing the beans through rolls is then conveyed to presses where it is subjected to tremendous pressures which remove the greater part of the oil. The flour is then prepared from the resultant cake which still retains about 5 percent of oil. In the solvent extraction method, the properly cleaned, steam-treated beans are granulated by means of reduction rolls, the hull particles removed, and the bean granules are then pressed into extremely fine flakes by passage between closely spaced cylinders. These soya flakes are then conveyed to the extractor where the oil is removed by a solvent, usually hexane, on a counter-flow principle, yielding extracted flake with an oil content of 0.5 to 1.0 percent and a protein content of 44 percent. After further treatment, these flakes are then ground into flour. Depending upon the treatment accorded to soya flour, its color will vary from pale cream to pale yellow.

Except for specialty breads, soya flour in bread making is used in relatively small amounts, the most frequently recommended quantities being from 1 to 5 percent based on wheat flour. The practical utilization of

soya flour in bread, cakes, yeast raised sweet goods, pies, etc., has been discussed by numerous writers, such as Bailey, Capen and LeClerc (*219*), Hafner (*222*), Trempel (*229*), Bohn (*230*), Faulkner and Simpson (*231*) and others. This literature is readily available and will hence not be reviewed here. The use of soya flour in bakery products has been advocated both for reasons of nutrition and of the beneficial effect of this ingredient upon the physical quality of the baked product. Thus, Hafner (*222*) summarizes the advantages attributed to the use of soya flour as follows: (1) Prolongs shelf-life of the baked product by (a) reducing the rate of evaporation of water from crumb (dehydration); (b) slowing down the interchange of water between starch gel and gluten in the crumb (staling); (c) inhibiting break-down of the shortening and other fats due to the anti-oxidant effect of soya phosphatides (rancidity). (2) Improves crumb structure by effecting a more even distribution of ingredients throughout the dough. This results in a more uniform expansion of the dough. (3) Imparts "body" or firmness to the crumb and reduces tendency toward doughiness. (4) Produces a fine textured crumb which toasts to a uniform, golden brown color. (5) Increases the nutritional quality of the protein to the extent that it is made equal or superior to protein of whole wheat bread.

PEANUT FLOUR

Although attempts were made as far back as 1920 (*232*) to develop a satisfactory bread containing relatively large proportions of peanut flour, these early ventures to popularize this product as a baking adjunct met with little commercial success. This failure was due largely to the generally unacceptable quality of commercially available peanut flours which were frequently considered mere by-products by peanut processing plants whose principal interest was in the peanut oil and press cake. Peanut flours offered to bakers prior to 1939 were little more than slightly refined peanut meals containing about the same quantities of grit, hair, hulls, and other foreign materials usually present in the meals used for feed. Also the flavor and the color proved generally unacceptable. It was not until 1939 that a process was developed for the manufacture of a peanut flour that met the requirements of flavor, color, freedom from foreign material, nutritional characteristics and processing costs. The processing methods are similar to those employed in soya flour production, involving selection of high quality peanuts, shelling and cleaning, oil extraction by either the expeller or solvent method, and grinding and bolting. Payne (*232*) lists the following tentative specifications of the peanut flour available from the process now in use:

"*Low fat peanut, food flour.*—Hulls and skins removed; free from par-

ticles of hair, insect fragments, or other foreign material; light in color, bland and free from any bitter or raw taste; less than 3 percent fiber; not less than 5 percent or more than 9 percent fat; not less than 55 percent protein with protein content specified; not more than 10 percent moisture; and not less than 95 percent through 120-mesh U. S. Standard screen."

The same author gives the following proximate composition of such a flour made from white Spanish-type peanuts:

TABLE 70. PROXIMATE COMPOSITION OF PEANUT FLOUR

		Range
Protein	60.0%	55-62%
Fat	7.0%	5-9%
Fiber	2.5%	2-3%
Water	6.0%	2-10%
Thiamine	4.0 I.U./g.	
Niacin	350γ/g.	
Riboflavin	5.0γ/g.	

The two principal proteins of peanut flour have been identified by Johns and Jones (*233*) to be globulins which they named arachin and conarachin. These two globulins, which are present in the ratio of 3 to 1, respectively, constitute about 85 percent of the total nitrogen present in peanut meal. Jones, cited by Geddes (*136*), gives the following amino acid composition for these two proteins.

TABLE 71. AMINO ACID COMPOSITION OF PEANUT PROTEINS

	Arachin	Conarachin
Glycine	0.0%	—
Alanine	4.1	—
Valine	1.1	—
Leucine	3.9	—
Isoleucine	—	—
Proline	1.4	—
Phenylalanine	2.6	—
Tyrosine	5.5	—
Serine	5.2	—
Threonine	2.6	2.0
Methionine	0.5	3.0
Aspartic acid	5.6	—
Glutamic acid	19.5	—
Arginine	13.5	14.6
Histidine	1.9	1.8
Lysine	5.0	6.0
Tryptophane	0.9	2.1
Cystine	1.5	4.4

TABLE 72. COMPARATIVE COMPOSITIONS OF PEANUT FLOUR, WHEAT FLOUR, AND MIXTURES OF THESE FLOURS

	Patent flour	Enriched flour	Peanut flour	25% Peanut 75% Patent
Protein, g/100 g..................	10.5	10.5	60.0	22.8
Ash, g/100 g.....................	0.42	0.42	4.6	1.5
Calcium, mg/100 g................	16.0	16.0	80.0	32.0
Iron, mg./100 g..................	0.8	3.6	2.4	1.2
Thiamine, I.U./g.................	0.2	1.7	3.0	0.9
Riboflavin, γ/g.................	0.51	0.51	4.0	1.5
Niacin, mg/100 g................	0.8	4.1	19.0	5.4

These values show that peanut flour, in common with soya flour and cottonseed flour, has a considerably higher content of essential amino acids than the cereal flours. When its generally high protein content is taken into account, it is rightfully considered as a rich source of indispensable dietary factors.

No accurate data concerning the use of peanut flour by the baking industry are available. It was reported in 1941 that some commercial

TABLE 73. AVERAGE PROXIMATE COMPOSITION OF COTTONSEED FLOUR

Chemical Composition:

Moisture..................	6.3%
Protein..................	57.5%
Fat......................	6.5%
Fiber....................	2.1%
N-free Extract............	21.4
Ash......................	6.2

Vitamins:

Thiamine, γ/g............	10.4
Riboflavin γ/g............	10.2
Niacin γ/g................	85.0
Pantothenic acid γ/g.......	25.5

Minerals:

Calcium...................	0.2%
Magnesium................	0.65%
Phosphorus................	1.30%
Iron......................	0.012%

bakers in at least one southern state were producing bread made from a flour mixture consisting of 75 parts of patent flour and 25 percent peanut flour. The comparative compositions of the various flours shown in Table 72 indicate the extent to which 25% additions of peanut flour to wheat flour modify the latter's composition (*234*).

The bread made with such high admixtures of peanut flour was characterized by a greatly reduced loaf volume and a dark and rather coarse-grained crumb. Bread of this type enjoys little acceptance in the United States.

COTTONSEED FLOUR

Acceptable cottonseed flour, obtained by grinding and bolting the cottonseed meal which remains after the oil has been removed, has been commercially available for a relatively short period. As a result practical experience with this product as a baking adjunct is still limited.

Cottonseed flour, when compared with cereal flours, is relatively high in its protein, fat and ash contents, and low in its carbohydrate content, as is apparent from the values reproduced in Table 73 from figures cited by Geddes (*136*). The product is also a rich source of the nutritionally important B vitamins.

The protein of cottonseed has been shown to consist of globulins, a pentose-containing protein, and a glutelin. Its amino acid composition is given in the following table, based on values compiled by Jones.

TABLE 74. AMINO ACID COMPOSITION OF
COTTONSEED PROTEIN

	%
Glycine	1.2
Alanine	4.5
Valine	present
Leucine	15.5
Isoleucine	—
Proline	2.3
Phenylalanine	3.9
Tryosine	2.3
Serine	0.4
Threonine	—
Methionine	—
Aspartic acid	2.9
Glutamic acid	17.6
Arginine	13.5
Histidine	3.5
Lysine	4.3
Tryptophane	2.6
Cystine	1.1

In comparing the general average compositions of soya, peanut and cottonseed flours, the rather striking similarity of their analyses is apparent. All three flours are characterized by a high protein, fat and mineral content, and a low carbohydrate content. Their proteins possess superior biological value and the flours are rich sources of essential min-

erals and vitamins. When first made commercially available, their inclusion in bread and other baked products was urged on the basis of their high nutritive value which in many respects approaches that of milk. The basic limiting factor to their extensive adoption in bakery production is the fact that when sufficient amounts of these adjuncts are introduced into bread to be nutritionally significant, they affect the baking characteristics of the dough and the quality of the finished bread. Additions exceeding 5 percent based on wheat flour will produce noticeable effects upon the appearance and palatability of the finished product which not all consumers find equally acceptable.

POTATO FLOUR

Potato flour has long been used in bread baking for various purposes: as an extender of wheat flour when the latter was in short supply during periods of economic emergency; as a flavoring agent to impart to white bread the distinctive flavor developed by potato during baking; as a staleness retarding agent after it was observed that small increments of potato flour tended to reduce the rate at which bread crumb became firm; and as part of the leaven prior to the introduction of compressed yeast when a typical "ferment" might consist of flour, mashed potato, hops and water.

The average composition of fresh raw potato on an "as is" and a dry basis is given in the following table, adapted from Kent-Jones and Amos (153).

TABLE 75.   AVERAGE COMPOSITION OF FRESH
POTATO

	As is Basis %	Dry Basis %
Moisture......................	75	—
Protein.......................	2	8
Available carbohydrates........	20	80
Fat, fiber, etc.................	3	12

If the dry basis composition of potato solids is compared with that of wheat flour solids, it will be noted that the difference in both carbohydrate and protein contents is not too great. Moderate additions of potato to bread, as is practiced in the production of potato bread, do not, therefore, diminish the nutritional value of the final product appreciably. In addition, potato flesh is superior to white flour in its contents of thiamine, riboflavin and niacin. The raw potato is considered a good source of Vitamin C, which is absent from wheat flour. However, there appears to

be some destruction of Vitamin C in the processing of potato flour so that this product contains only traces of this vitamin.

Potato flour, which is the normal form in which potato is at present used in the bakery, may be made in several ways. In one process, the potatoes are freed from foreign matter, washed, and passed through a steam cooker on a conveyor belt in which they are subjected to cooking by superheated steam under pressure. They then pass into an extruder which removes the skins and from there are fed between hot iron rolls which dehydrate the potatoes and press them into flakes. The flakes are then milled either into fine or granular flour. In another method, the cooked potatoes emerging from the extruder are fed into a tank where water is added to make a liquid. This liquid is then pumped at high pressure through spray atomizers into a drying chamber in the form of a fine mist. The mist is met by a blast of heated air which instantaneously dries the droplets, permitting the potato solids to drop to the bottom of the spray chamber as a fine powder. A third method involves peeling the potatoes by machine, cutting them into slices, drying the slices by passage through tunnel driers and then grinding the dried material into flour. It should be noted that the last process yields a product which is still in a raw state.

A typical analysis of a commercial sample of cooked, peeled potato flour, as cited by Treadway (235), is as follows:

TABLE 76. COMPOSITION OF POTATO FLOUR

	Percent
Moisture	7.2
Ash	3.2
Protein (N × 6.25)	8.0
Fat	1.4
Crude Fiber	1.6
Carbohydrate	78.7
Calcium	0.03
Magnesium	0.10
Potassium	1.59
Sodium	0.04
Iron	0.03
Copper	0.001
Phosphorus	0.18
Sulfur	0.12
Chlorine	0.12
Silicon	0.01

It will be noted that more than three-fourths of potato flour solids represent carbohydrate which occurs in the form of gelatinized starch and

is hence readily attacked by amylolytic enzymes and converted into fermentable sugars. This is one of the reasons why potato flour generally exerts a marked accelerating effect upon dough fermentation. Another is the fact that the proteins of potato are to a large degree soluble and are thereby available for assimilation by the yeast which utilizes them for rapid growth. Potato flour also contains growth promoting mineral substances, particularly potassium, magnesium, and phosphorus, which stimulate yeast development and promote active fermentation.

Potato flour should be distinguished from potato starch flour, as the latter product is pure potato starch and does not contain the protein, fat, and mineral constituents which are present in whole potato and which are retained in potato flour.

Mention should also be made of sweet potato starch which in recent years has become commercially available and has found limited utilization in the baking industry as a bread improver. This product, which is sold as a white powder, is characterized by a rather high amylose content and greater than average capacity to absorb and tenaciously hold water (*236*). Analyses of a great number of typical samples have given the average results shown in the following table.

TABLE 77.   COMPOSITION OF SWEET
POTATO STARCH

Ash..........................	0.17%
Solubles.....................	0.20
Moisture....................	12.00
Carbohydrates...............	87.60

The use of sweet potato starch, in an amount of 1 percent, is recommended especially with high-protein flours.

CHAPTER X

SUGARS AND SYRUPS

Sugars and syrups rank among the primary ingredients used in the production of a wide variety of baked goods. The importance attributed to them rests upon their multiple functions as highly desirable nutrients, sweetening and flavoring materials, stabilizing agents, and fermentation controllers. For these reasons, a basic understanding of the principal chemical, nutritional and technological properties which govern their behavior in baking is essential if they are to be used to the best advantage.

Modern science and technology have made available to the baking industry an extremely wide range of types and varieties of sugars on a commercial scale which gives the baker full scope to practice his craft. The chemical composition and characteristics of the principal types of sugar have been outlined in the main in the chapter on The CARBOHY-DRATES. The present discussion will therefore confine itself to the manufacture of sugars, their characteristics as primary baking ingredients, and their functional behavior.

SUCROSE

Cane Sugar Manufacture. By far the most important of commercial sugars is sucrose, obtained principally from the sugar cane and the sugar beet. All other sources of sucrose, such as the sweet sorghum, maple sap, and various species of tropical palm trees, are of relatively minor significance.

While basically the methods of extracting and processing sugar from the various sugar containing plants are the same, they vary in significant details depending upon the type of raw material used, the technological status of the sugar processing plant, and consumer preference. In the following paragraphs the discussion will deal mainly with the manufacture of cane and beet sugar.

Sugar cane at harvest time contains from 16 to 20 percent sucrose (cane sugar), in addition to small amounts of other types of sugar, mineral and organic matter and coloring and flavoring substances. The woody stalks of the sugar cane are delivered to the sugar mill where they are cut into small segments, crushed and their juice extracted. The liquid obtained is then passed through strainers and run into settling tanks where the coarser suspended material settles out. The juice is then transferred into

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mixing tanks and treated with sulfur dioxide and lime which further act to precipitate many of the impurities. From there the clarified juice is run into evaporators where it is concentrated into a thick and viscous syrup. Further concentration is obtained by evaporation in vacuum pans until the syrup is saturated with sugar and crystallization sets in. Concentrated syrup is then added to increase crystal size by deposition of sugar on the crystals already formed. The crystal-syrup mass, called massecuite, is transferred into centrifugal baskets which separate the crystals from the mother liquor, yielding raw sugar and first molasses, both of which are commercial products. The raw sugar obtained at this stage is a brown, coarse-textured product containing some 97 percent of sucrose and traces of syrup; other types of sugar, organic and mineral impurities, and moisture. Practically all of the raw sugar is subjected to further refining and very little of it reaches the market in its original form.

The first molasses, if not sold as such, is then returned to the vacuum pan for further concentration, to be followed by another centrifugation which extracts additional sugar crystals and yields a so-called "second molasses" of lower sugar content and a higher content of such impurities as mineral salts, simple sugars, gums, and organic acids. It also may either be sold as such or subjected to further concentration and centrifugation. The final molasses or "blackstrap molasses" obtained after the third extraction has a sugar content too low to make further processing economically desirable. It is usually considered non-edible and is utilized by industries other than the food industries.

In addition to molasses, the cane sugar industry, as distinct from the sugar refineries, produce two other sugar products which are marketed directly. One is turbinado sugar, a product somewhat purer than ordinary raw sugar and therefore lighter in color. It is readily soluble and because of its lower cost is used to some extent in the baking of darker colored products such as cookies, certain types of cakes and sweet goods, etc. The other sugar product made directly for the consumer market is the so-called "plantation granulated sugar" or "plantation whites," whose processing resembles the method employed in beet sugar manufacture. It lacks the pure whiteness of standard granulated sugar and, what is of far greater importance, is deficient in uniformity of quality, different samples varying according to crop, soil, raw materials used in manufacture, etc. Neither of these two sugar products are made in great quantities and they are therefore of relatively little commercial importance.

Beet Sugar Manufacture. The sugar beet today represents the second most important source of refined sugar. Beet sugar manufacture was first attempted some 200 years ago with relatively little initial suc-

cess because of the low sugar content of the beets originally used. Subsequently, however, it has proved possible to develop a strain of beets containing as much as 18 percent of sugar when ripe. In sugar extraction, the washed beets are sliced into thin strips and transferred into diffusion cells where their soluble substances are extracted with hot water. The liquid obtained in this manner contains approximately 12 percent of sugar in addition to many organic and inorganic impurities which impart to it a dark color. The juice is first strained and then treated with lime and carbon dioxide which form a precipitate which in settling out carries with it practically all of the impurities. The treatment may be repeated several times until a clear, pale yellow filtrate is obtained which is subjected to a final clarification with sulfur dioxide, and is then ready for evaporation and crystallization. The clear syrup yields white sugar crystals which are separated by centrifugation, washed, dried, and packed for market. The mother liquor is then given further treatments to exhaust its sugar content more completely.

Refining of Sugar. Sugar refining performs a two-fold task: the conversion of raw sugar into pure sucrose and the production of sugar varieties especially suited for the specific requirements of the sugar using industries. Raw sugar delivered to refineries is first purified by a series of treatments which remove the molasses adhering to the raw sugar crystals as well as all other impurities. This results in a water-clear syrup from which a large variety of sugars, varying mainly in their grain sizes, are obtained by careful processing. The most common varieties offered to industrial sugar users include the following:

"Coating Sugar"—an extremely finely granulated sugar used principally for coating pan goods in the production of confectioneries.

"Bakers Special"—a sugar of very fine grain consisting of whole crystals and therefore better suited for cake making than powdered sugar.

"Fruit Granulated"—a very finely granulated sugar designed for dry mixing with finely dispersed substances. It is also highly suitable for cake making.

"Extra Fine Granulated"—a general purpose industrial sugar, intermediate in fineness of grain between Fruit Granulated and Fine Granulated Sugar.

"Fine Granulated"—a sugar of uniformly fine crystal size. It is the type used primarily by bakers and confectioners as a sweetening agent.

"Sanding Sugar"—a sugar of unusually uniform grain size and brilliant luster, suited especially for sprinkling on cookies and sweet goods.

"Medium Fine Granulated"—a sugar of somewhat larger grain size than Fine Granulated sugar. It is preferred by many as a general purpose sugar.

"Medium Granulated"—a sugar of exceptionally pure color having a grain size larger than Medium Fine Granulated sugar but smaller than Standard Granulated sugar.

"Standard Granulated"—a sugar which is readily soluble especially where heat can be applied to the solution. It is also used for grinding purposes.

"Coarse Granulated"—a sugar of very large grain used in specialty products in which the original sugar crystals contribute to the special effect of the finished item, such as sugar-sprinkled cookies and cakes.

In all of the above enumerated sugar types the variation in grain size is achieved by a judicious control of the crystallization process. The crystals are separated from the mother liquor by centrifugation, washed and dried and then passed over sieves for separation according to size.

The so-called powdered sugars are obtained by grinding coarse granulated sugar in special mills and screening through fine bolting cloths. In order to prevent caking, 3 percent of finely pulverized corn starch is mixed in with the powdered sugar. More recently, tri-calcium-phosphate in 1 percent increments has found application as an anti-caking agent in powdered sugar. The product is available in the following commercial grades:

"Confectioners XXXXXX"—a pulverized sugar of extremely fine texture, especially suited for sugar fillings.

"Confectioners XXXX"—a fine textured, pulverized sugar used principally for uncooked icings and for dusting purposes on pies, pastries and similar products.

"Standard Powdered"—a sugar less finely ground than Confectioners XXXX and suitable for use where extreme fineness is not essential.

"Coarse Powdered"—a sugar of coarser texture than Standard Powdered and used when too fine a texture is undesirable as, for instance, in coating of doughnuts.

A relatively new type of sugar introduced by the refining industry is the so-called "transformed sugar." This product is neither a crystalline product nor a powdered product. It is produced by flashing the clarified sugar syrup into an agitation chamber in superheated form. The resulting sugar particles, which range in color from white to dark brown depending upon the color of the syrup, are of a very irregular shape with numerous cracks and crevices. The sugar crumbles very easily and dissolves almost instantly. Because of the irregular grain structure, the sugar is highly aerated and is particularly suitable for creaming with shortening in cake making. The transformed sugars act similar to leavening agents and when used will reduce the quantity of leavener required to produce a given amount of aeration.

The so-called soft sugars, which range in color from white to dark brown, are obtained by so conducting the crystallization process that a relatively large amount of the mother liquor remains occluded to the sugar crystals formed. In certain of the lower grades, as much as 25 percent of the soft sugar may consist of uncrystallizable simple sugars. The soft sugars readily absorb and retain moisture and possess a very pleasant flavor. They are graded according to color, No. 1 being nearly pure white and No. 15 having the color of roasted coffee. The grades primarily used in baking range from No. 6, which has a light yellow shade and is used in lighter colored bakery goods, to No. 13, a dark brown sugar used in such products as rye bread, ginger bread, etc. The use of these soft sugars is further favored by their relatively low cost.

In more recent years the so-called "liquid sugars" have appeared on the market. These are highly concentrated solutions of pure sucrose ranging in color from water-white to light amber. Their main advantage is their economy, since they are shipped in bulk in glass-lined tank cars and obviate the need for bagging, handling, storage and dissolving.

Refiners syrup, a by-product of sugar refining, consists of the residual mother liquor which, in its commercial form, contains not more than 25 percent of water and 8 percent of mineral matter, the remainder being made up of sugars. It ranges in color from nearly colorless to dark brown and has a flavor similar to that of molasses, though not quite as pronounced. It is used commercially as a substitute for molasses as well as in the blending of molasses.

INVERT SUGAR

When sucrose is boiled with dilute acid it is hydrolyzed into its constituent sugars, glucose (dextrose) and fructose (levulose). This mixture of sugars differs in several respects from the original sucrose. Thus whereas sucrose has a positive optical rotation of $+66.4°$, the resulting mixture has a negative rotation of $-39°$. Because of this change from dextrorotation to levorotation, the hydrolysis is called inversion and the resulting product invert sugar. Inversion of sucrose takes place also in dough fermentation where it is brought about by the yeast enzyme invertase. Inversion also produces a change in sweetness. The sweetness of sucrose has been arbitrarily designated as 100. Using this value as a base, levulose or fructose is found to possess a sweetening power of 173 and dextrose of 74. Their combined sweetening power in a completely inverted sugar in which both of the constituent sugars are present in equal proportions approximates 127 on a dry weight basis. In the form of a syrup containing 75 percent total sugar its sweetness is about that of pure dry sucrose.

Invert sugar is used principally for its high hygroscopicity, i.e., its pronounced ability to absorb moisture. Thus bakery products in which invert sugar is used in relatively large amounts, such as cookies, layer and pound cakes, icings and pastes, remain moist for prolonged periods. The actual percentage of invert sugar to be used depends upon the type of product and the characteristics aimed at. Thus in certain types of cookies all the sweetener called for in the formula may advantageously consist of invert sugar, while in others 25 to 50 percent will yield best results. When used in pound and layer cakes, experience has shown that optimum results are obtained when invert sugar is limited to less than 10 percent of the total sugar increment.

While invert sugar syrups of uniform quality are available commercially, such syrups are readily prepared in the bakery by the use of equipment generally available. Although any type of kettle may be used in which to carry out the inversion, a jacketed kettle which can be heated with steam and cooled with water and is equipped with an agitator will be found most convenient. One hundred pounds of purified granulated sugar, either beet or cane, is placed in the kettle and approximately 33 to 35 percent of water, based on sugar weight, stirred in. To this sugar concentrate is added 2 ounces of tartaric or citric acid. The steam is then turned on and the batch brought to a boil. Since a sugar solution of such concentration has a boiling point of around 225° F., steam pressure of some 20 to 25 lbs. will be required to attain the desired temperature. The batch is allowed to boil slowly for 30 minutes under constant agitation and is then quickly cooled to 100° F. by running cold water through the kettle jacket. There are many variations of this procedure. Thus some bakers add the acid component to the water prior to its addition to the sugar, while others wait until the sugar concentrate has reached the boiling point. Similarly, some prefer to boil the batch for a predetermined time, while others prefer to cook to a definite temperature, usually around 234° F. Most of these variations are in the nature of concessions to different types of equipment available for this process. When lower grades of granulated sugar are used, the acid increment generally required is slightly higher if complete inversion is to be obtained because of the presence of buffer substances in the sugar which render part of the acid ineffective. Generally a syrup having a pH value of 2.5, and a moisture content of 22 to 23 percent is obtained. Under ordinary conditions and for most purposes for which invert syrup is normally used, it is not necessary to neutralize the acidity of the syrup. Should this acidity prove too high, as it would if relatively large proportions of sugar are to be replaced by the invert syrup, it may be reduced by the addition of 1 ounce of sodium bicarbonate per 100 lbs. of sucrose used originally.

Aside from its hygroscopic character, which is the principal reason for its use in baked goods, invert sugar has also been found to produce a quicker bake and coloring, to impart a pleasing flavor to the products, and, in the case of drop cookies, to improve the spreading action of the batter. Its resistance to crystallization and its ability to prevent or reduce crystallization in other sugars is also desirable in extending the shelf-life of cakes and cookies.

Some care is required in the use of invert sugar for best results. Thus one producer of commercial invert syrup has released the following recommendations for the various products listed below (*237*):

Product	Recommended percent of invert sugar based on total sugar used
Pound cakes	0.3-7.5%
Fruit cakes	
light	10%
dark	10% or more
Batter cakes	
white	7.5-10%
gold	7.5-15%
chocolate and other dark cakes	10-30%
Sponge cakes	
loaves and rings	5.0-7.5%
layers, jelly rolls and small units	7.5-15%
Cookies	
crisp	5%
chewy	10%
soft	15%
Yeast raised sweet goods	20-50%
Icings—wrapped	2.5-10%
unwrapped	10% or more
Marshmallow	10-50%

Weiss (*238*) has recently reviewed the role of sugar in baking in a series of detailed articles. During fermentation yeast encounters four fermentable sugars in the dough, namely, the two disaccharides maltose and sucrose, and the two monosaccharides glucose and fructose, which are derived from sucrose on inversion by the yeast enzyme invertase. Glucose is also added extraneously in the form of pure corn sugar. Yeast ferments these sugars at a rate which varies with each individual sugar. Thus glucose is converted most rapidly into carbon dioxide and alcohol. Fructose is fermented at a rate of about one half that of glucose and its fermentation is initiated only after the greater part of glucose is exhausted. Yeast, therefore, shows a selective action, preferring glucose to fructose as a fermentable substance. Rice (*239*), who investigated this

subject more than a decade ago, suggests the following mechanism of sugar conversion: The yeast cell first absorbs sucrose, inverts it by means of invertase into glucose and fructose, with the glucose being metabolized immediately, while fructose is excreted by the cell. When the available glucose has been used up, the yeast then reabsorbs the fructose. He found that when approximately 6 percent sucrose was added to a dough, about 76 percent, or two-thirds, was consumed by the yeast, and that the residual sugar consisted principally of fructose. Fructose differs markedly from glucose in several important respects, being superior in its sweetening power, moisture retaining capacity, and its ability to caramelize at elevated temperatures. Hence, from a quality standpoint, it is more desirable to have the residual sugar consist of fructose than of glucose. Maltose is fermented at the slowest rate, there apparently existing an induction period. Like sucrose, maltose must also first be inverted by an enzyme maltase into glucose which is then directly fermented.

DEXTROSE AND CORN SYRUPS

Dextrose and Acid-Converted Corn Syrups. A series of widely used syrups and sugars are produced commercially by hydrolizing starch, generally corn starch in this country, with hydrochloric acid. Very briefly, the products thus produced may be listed as follows:

1. Syrups of purities (reducing sugars expressed as percent of dextrose on dry basis) from 25 to about 55. These are referred to as corn syrup, unmixed (C.S.U.). Such syrups, when designed for use by bakers, have a purity within the range of 40-43. They are heavy, clear, white viscous liquids containing in addition to dextrose also maltose and some dextrines.
2. Syrups of purities between 63-65, generally referred to as high sweetness syrups.
3. Crude sugars of purities between 70 and 80, known commercially as "70" and "80" corn sugars.
4. Refined dextrose hydrate (purity about 99.5) with an average moisture content of 8 percent.
5. Refined anhydrous dextrose (purity approaching 100) with a moisture content of 0.2 percent.

The comparative composition of sweetening agents, including the principal sugars and syrups derived from corn starch, are given in the first part of Table 78. The second part lists the proportions of the various sugars which are present in these sweetening agents (240).

While methods of acid hydrolysis of starch differ in the production of the various corn derivatives, the initial phases in all cases are essentially the same. A starch slurry at about 20-22° Bé. is acidified with hydrochloric acid to a pH of about 1.8 to 2.0 and pumped into closed cylindrical vessels which serve as converters. This process of charging, which

TABLE 78. COMPARATIVE DATA ON SWEETENING AGENTS

| | (Analysis usually reported) | | | | |
Type of Sugar	Moisture Average	Ash	Purity*	Sweetness Range	Misc.
Sucrose....................	0.2 max.	.02	—	100	—
Brown sugar..............	2.5	.65	—	95 to 100	1.10†
Dextrose-hydrate..........	8.0	.03	99.5	75 to 80	—
Dextrose-anhydrous........	0.2	.02	99.8	70 to 75	—
Honey....................	12.0	.30	74.0	75 to 80	5 to 6‡
Corn syrups (high sweetness).	18.0	.20	63–65	45 to 50	—
Regular gravity corn syrup					
unmixed................	18.0	.30	40–43	25 to 30	—

| Average Proportion of Sugars on "as is" Basis | | | | | |
Type of Sugar	Sucrose	Dextrose	Levulose	Maltose	Dextrines
Sucrose.......................	99.7	—	—	—	—
Brown sugar..................	90.0	2.0	2.0	—	—
Dextrose-hydrate.............	—	91.8	—	—	—
Dextrose-anhydrous...........	—	99.5	—	—	—
Honey.......................	5.0	36.0	38.0	—	3.0
Sweet corn syrup..............	—	32.8	—	32.8	16.4
dry basis...................	—	40.0	—	40.0	20.0
CSU.........................	—	18.5	—	25.0	36.5
dry basis...................	—	23.2	—	31.2	45.6

* Reducing sugars on dry basis
† organic matter
‡ undetermined

requires about 10 to 15 minutes, is so graduated that the starch is gelatinized and converted without giving rise to the formation of large lumps of paste. A conversion temperature of 132 to 137° C. is employed (obtained by heating under pressure) and normally conversion is completed within 20 to 30 minutes after initiation of the process. When the desired degree of conversion has been attained, the liquid is transferred to a neutralizing tank and treated with sodium carbonate to neutralize the hydrochloric acid. This is followed by a series of filtrations and evaporations under vacuum until the desired syrup concentrations are attained. If dextrose is to be produced, the concentrated solutions are made to crystallize by seeding with a small amount of anhydrous dextrose and by lowering the temperature; the dextrose crystals thus formed are centrifuged off, washed, dried and packed.

Refined dextrose is a crystalline, white product possessing a sweetness of about three-fourths that of sucrose. The pure dextrose crystals of commerce are available in two basic forms, hydrate and anhydrous. The hydrate form, more generally used in baking, is supplied in three crystal sizes: (1) "Regular" with approximately all passing through a 14 mesh screen; (2) "Powdered," passing through a 48 mesh screen; and (3) "Pul-

verized" with nearly all through a 200 mesh screen. These different crystal sizes are designed to provide progressively more rapid rates of solubility. Thus the "Regular" crystal size will be found suitable for all bread and sweet doughs, and for such cake and cookie work where the mixing time and water content of the dough or batter are long and high enough, respectively, to ensure complete solubilization of the dextrose. "Powdered" and "Pulverized" dextrose forms are limited in their use principally to cake and cookie production and the formulation of icings and toppings where a high degree of solubility is either desirable or actually required.

Dextrose differs in several respects from sucrose. It crystallizes more slowly, is less soluble in water, has a higher osmotic pressure and is less sweet than sucrose. Being directly fermentable by yeast, it is especially able to support yeast growth during fermentation. It caramelizes at a lower temperature and pH than sucrose and thereby contributes to the production of good crust color and toasting qualities.

A variety of corn syrups, obtained by acid hydrolysis of corn starch, find extensive use as sweetening agents in baking. The syrups are relatively thick, viscous liquids containing in solution dextrose, maltose, higher sugars and dextrines. The proportion of these component sugars is largely dependent upon the degree of hydrolysis to which the original starch was subjected. A typical comparative analysis of "Normal" (CSU) and "High Conversion" (high sweetness) syrups is given in the following table (*241*):

TABLE 79. COMPARISON OF "NORMAL" AND "HIGH CONVERSION" SYRUPS

	Normal Syrup	High Conversion Syrup
Moisture......................	20%	20%
Dextrose.....................	22% (dry basis)	43% (dry basis)
Maltose......................	21% " "	29% " "
Higher sugars................	20% " "	6.5% " "
Dextrines....................	37% " "	21.5% " "
Dextrose equivalent..........	43	62

The three principal types of corn syrup available are "low," "normal" and "high conversion" syrups. Their respective dextrose equivalents, which bear a direct relationship to their dextrose and maltose contents, are 30, 43, and 62. Syrups of 43° Bé. are generally used, although somewhat lighter syrups may be preferred by some users because of their easier handling at the low temperatures encountered during the winter months.

Corn syrups are used largely for their stabilizing properties and their

humectantcy or moisture retaining capacity. In such products as icings and toppings which are exceptionally high in sugar content, the corn syrups prevent or reduce the graining or crystallization of other sugars, notably of sucrose, and retain a desirable degree of moisture. Syrups in amounts of 1-2 percent based on flour are said to retard the rate of practical staling (*241*) although they have no effect upon the rate of chemical staling. Corn syrups are used extensively in the production of cakes, cookies, cup cakes and similar items whose shelf-life is markedly prolonged by the humectantcy of the syrup. Large amounts are also used in fruit pie fillings and jams and jellies prepared for baking purposes.

Enzyme-Converted Corn Syrups. In addition to regular acid-converted corn syrups, a new type of syrup obtained from refined corn starch by conversion with enzymes has been introduced on the market in 1939. The product, known commercially as Sweetose, is a clear, hygroscopic syrup, devoid of practically all flavor other than sweetness. It is non-crystallizable and tends to reduce crystallization of granular sugar. Its composition, in comparison with regular corn syrup, is given in the following table (*243*):

TABLE 80. COMPARATIVE COMPOSITIONS OF ENZYME- AND ACID-CONVERTED CORN SYRUPS

	Enzyme-Converted Corn Syrup 43° Baumé	Acid-Converted Corn Syrup 43° Baumé
Moisture	18.2%	19.7%
Total solids	81.8%	80.3%
Dextrose	30.6%	17.6%
Maltose	27.9%	16.6%
Higher sugars*	13.1%	16.2%
Dextrines	9.9%	29.6%
Ash	0.3%	0.3%
Dextrose Equivalent**	63.0%	42.0%
pH	4.9-5.1%	4.9-5.1%
Viscosity (at 100° F)	58 poises	150 poises
Weight per gallon	11.82 lbs.	11.82 lbs.
Boiling point	233.5° F.	227.3° F.

* Maltotriose and maltotetrose
** Total reducing sugars on a dry basis, calculated as dextrose.

From these comparative figures it is seen that the enzyme-converted syrup contains some 87.5% of sugars based on total solids, compared with 62.7% for regular corn syrup. While the sugar content differs only by 24.7%, the enzyme-converted corn syrup is about twice as sweet as the acid-converted syrup. The relative order of sweetness of these syrups as

compared with other sweeteners is apparent from the following table (*243*):

<div align="center">

TABLE 81. RELATIVE SWEETNESS OF
SUGARS AND SYRUPS

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Sucrose	100
Dextrose	75
Enzyme-Converted C.S.	60
Corn Syrup (CSU)	30
Maltose	30
Lactose	15

In addition to its greater sweetness, enzyme-converted corn syrup differs from acid-converted corn syrup in several other respects. Its viscosity at 60° F. is only about one-third that of regular corn syrup. This means that the product is rather free-flowing at only slightly higher than normal temperatures so that it can be handled with relative ease either through pipe lines, or from tanks or drums. The enzyme-converted syrup further possesses a nearly pure sweet taste, being almost devoid of other flavors. This characteristic allows its use in instances where strongly flavored sweeteners are undesirable. Also it can be used in fairly large proportions, either as a complement to sucrose or as a substitute for it. When used in combination with sucrose, it results in a sweetness of the mixture which is greater than the sweetness of the separate substances. In 25 percent solutions of sucrose, one-third of the sugar may be replaced with the syrup solids without effect upon the solution's sweetness. In such a combination with sucrose, the syrup solids have an apparent sweetness equal to that of sucrose (*243*).

The enzyme-converted corn syrup finds extensive use in baking. It has been recommended as a sweetener or as a source of fermentable carbohydrate for a large variety of products. The following uses, with their advantages, have been suggested for it (*242*).

Bread, rolls or buns: Part or all of the sweetener may consist of the syrup to afford improved eating characteristics and longer shelf-life.

Sweet doughs: In these goods the syrup extends the keeping quality and produces softer texture.

Pie fillings: Part or all of the sweetener may consist of the syrup. Its use will improve the sheen or luster, the syrupy texture and body of pie fillings and intensify the natural fruit flavor.

Pie dough: In pie dough this sweetener will produce improved crust color, with resulting richer appearance and a speedier bake or faster browning, not only on the outer surface but throughout the entire crust.

Meringue: Because of its excellent whipping qualities, its use in meringues will improve stability and texture.

Cakes: In cakes part or all of the sweetener may consist of the syrup. It tends to produce improved crust color, to extend shelf-life, to afford a softer texture and better eating qualities.

Cookies: Its use produces easier spread, a rich crust color and more appetizing appearance and extended shelf-life.

Icings: In icings the syrup improves the sheen and appearance, accentuates flavors, and retains freshness. The amount recommended for any icing will depend upon the type, the manner in which the iced product is to be packaged, and upon the climatic conditions (more in dry cool weather, less in hot humid weather).

Its use has also been suggested for the production of such materials used by bakers as fudges and icing bases, marshmallow topping, jams and jellies, fondants, glace fruits, frozen fruits, frozen eggs and flavoring agents.

When part of sucrose is replaced by the syrup on the solids basis in a formula, the usual practice calls for $1\frac{1}{4}$ part of the syrup for 1 part of the sucrose and compensating for the moisture in the syrup by reduction of the liquid in the formula by 18 percent, or roughly $\frac{1}{6}$, of the syrup used.

HONEY

Honeys are classified for most commercial purposes according to their floral-nectar source. Thus, the four types of honey used extensively by bakers are known as orange blossom honey, clover blossom honey, sage blossom honey and buckwheat honey. Orange blossom honey is representative of the so-called white honeys, being a very light colored syrup. It possesses a fragrant aroma and a mild pleasing taste. Clover blossom honey may be classed as a light amber type with a slightly more pronounced fragrance and taste. Sage blossom honey is amber in color with a rather pronounced characteristic fragrance and taste. Buckwheat honey is a so-called dark honey with very strong aroma and taste and lacking the fine character of the other types mentioned. In general, the two latter types of honey are too dark in color and too pungent in flavor to be used in bread and light colored cakes, their use being restricted to the production of dark cakes and cookies and such specialty items as honey cakes and "Lebkuchen."

Honeys used for baking purposes should be relatively light in color and mild in flavor, except for specialty products where strong color and flavor may be preferable. They must be free from foreign material, such as wax, propolis, bees, bee fragments or dirt. Usually honey that has been strained through standard bolting cloth of 86 meshes per inch at a temperature of not more than 130° F. will satisfy the cleanliness require-

ment for bakery use. To prevent spoilage by fermentation induced by yeasts, the honey should not exceed 20 percent in moisture content and should be pasteurized to destroy the yeast cells. Heating to 140° F. and holding for 30 minutes at that temperature will generally suffice to produce sufficient sterility, according to Fabian and Quinet *(244)*. Such heat treatment also reduces the tendency of a given honey to granulate by dissolving the dextrose crystals which may have formed. This in turn also reduces the danger of fermentation by preventing the segregation of the honey into dextrose hydrate crystals of relatively low moisture and a thinner liquid portion of higher moisture content which is more susceptible to fermentation. Honeys must finally be free from objectionable flavor or odor.

Honeys from different sources vary considerably in their composition so that it is practically impossible to arrive at an acceptable composition for a typical product. A. C. Glabau *(245)* offers the following table as indicating the variations in the composition of honeys:

TABLE 82. RANGE IN COMPOSITION OF HONEYS

Water	12.43-26.07%
Invert sugar	69.17-75.09%
Sucrose	0.0 - 3.89%
Ash	0.12- 0.62%
Dextrine	0.26- 3.82%
Undetermined	1.15- 8.00%
Organic acid	0.10- 0.41%

G. P. Walton *(246)*, in discussing the composition of domestic honeys, suggests that the following approximate analysis might apply to an "average" domestic honey:

TABLE 83.   AVERAGE COMPOSITION OF HONEY

Moisture (adjusted)	18%	
Total sugars	76.4%	
Levulose		40.5%
Dextrose		34.0%
Sucrose		1.9%
Dextrines	1.7%	
Ash	0.18%	
Formic acid	0.1%	
Undetermined (by difference)	3.82	

The ratio of dextrose to levulose (fructose) is of considerable importance since the tendency toward granulation or crystallization of untreated honeys is closely reflected by this ratio. Honeys which contain a relatively large porportion of levulose in comparison to dextrose, i.e., in which the dextrose-levulose ratio is high, show a reduced tendency to

granulate. An example of such honey is tupelo honey from southeastern United States in which this ratio may approach 1:2, that is, it contains nearly twice as much levulose as dextrose. This honey seldom, if ever, shows signs of granulation.

A majority of commercial grades and types of honey are now processed by packers to improve their non-granulating character. This processing generally involves thorough liquefying and filtration, followed by pasteurization, to ensure that all traces of crystallized sugar have been redissolved.

While honey is not used extensively in white bread production, it nevertheless constitutes a suitable sweetener for such a purpose, as has been shown by Geddes and Winkler (*247*) and Lothrop and Bailey (*249*). Geddes and Winkler, on the basis of a rather comprehensive series of tests with honey in bread baking, particularly in relation to relative rates of gas formation from honey and sucrose in dough, concluded that honey and sucrose are of equal value for bread making purposes on the basis of sugar content. Lothrop and Bailey, using a standardized baking procedure, compared the effects of a number of different honeys with that of sucrose on bread characteristics. In their tests they used 3 percent sucrose, based on flour weight, in the control, and 4 percent honey of the following varieties: alfalfa-sweet clover, sweet clover, alfalfa, white clover, sweet clover-white clover blend, tupelo, ti-ti, light amber alfalfa, tulip-poplar, incense-cedar honeydew, and buckwheat, listed in the order of increasing color intensity. The results showed that only in the case of the three darkest honeys was the color of the crumb affected to a perceptible extent, and only in the case of buckwheat (darkest of the samples) was the effect sufficiently pronounced to render the bread unacceptable from the standpoint of color. With respect to volume, symmetry of form, evenness of bake, break and shred, grain, and texture, all test loaves proved entirely satisfactory. Only in the case of the most strongly flavored honeys, such as buckwheat, was it possible to detect any appreciable honey odor or flavor in the finished bread when 4 percent honey was used. The results of these baking tests indicate that honeys of a wide variety of floral type can be satisfactorily used in the baking of white bread when used in amounts comparable to the normal increments of sucrose on a sugar basis.

The same authors compared the relative hygroscopicity of honey with other saccharine liquids. They found honey to be more hygroscopic than commercial invert sugar syrup, much more hygroscopic than commercial corn syrup, but less hygroscopic than a syrup prepared from levulose, which however is not as yet a commercial article. Not all honeys are identical in their hygroscopicity. Differences in this property are

thought to be due more to variations in composition of certain non-sugar constituents, such as colloids and dextrines, than to variations in the proportion of the sugars present.

The moisture retaining property of honeys is also imparted to a limited degree to baked products in which honey is an ingredient. Moisture retention of cakes in which honey was used as the sole sweetening agent was much greater than in cakes made with other types of syrups. In the case of bread little difference on this point can be observed because of the very small amount of honey that can normally be used.

MALT AND MALT SYRUP

Malt syrup has long been used in bakery products, its superiority as a dough improver having been recognized in the early 1890's. In addition to the sugar maltose, malt syrup contains mineral salts, soluble protein, dough conditioning enzymes, and flavor and nutritive substances which promote vigorous yeast growth, hastening dough conditioning, and add distinctive flavor and aroma to the finished products.

While malt and malt syrup can be made from a variety of cereals, barley is used to the exclusion of nearly all other grains, excepting small amounts of wheat and corn. Selected varieties of barley, possessing the requisite characteristics, are employed. In malt production, the grain is first steeped in water to a predetermined moisture content, then permitted to germinate or sprout. Germination may be carried out either on a floor, in drums or in compartments. During this process the grain kernels begin to liberate amylolytic and proteolytic enzymes which act upon the starch and protein constituents of the grain, bringing about a partial conversion and modification. When germination has progressed to the desired degree, judged usually by the growth of the acrospire of the kernels, the so-called green malt is transferred on to kilns where it is subjected to drying at elevated temperatures. During kilning the moisture content is reduced from about 50 percent to less than 5 percent. If malt flour is to be produced, the dried malt is ground at this stage and is then ready for use.

The production of malt syrup requires additional processing. The malt is milled so that the individual kernels are thoroughly broken up. The ground malt is then transferred to large mashing tubs equipped with stirring devices and combined with tempered water. Here it is subjected to constant agitation for several hours, the temperature of the mash being increased gradually through several stages. During this treatment, the amylolytic enzymes are liberated from the malt and are able to liquefy the insoluble starches and convert them into maltose and dextrines. At the same time, the proteolytic enzymes act upon the high-

molecular protein substances, converting them into simpler soluble forms. Thus a malt extract, or wort, is obtained containing maltose, dextrines, solubilized protein substances, amylolytic and proteolytic enzymes, mineral salts and other soluble malt substances. This extract is then drawn off and separated from the insoluble malt husks and concentrated in large vacuum pans until a thick syrup results. It is transferred to finishing pans and the evaporation continued until the desired consistency is obtained. Depending upon the temperatures employed during this final treatment, syrups of high, medium or no diastatic activity result. Malt syrups offered to the baking industry may differ considerably in composition because of variations in processing procedure, differences in barleys used, and varying admixtures of starch raw material, such as corn, by different manufacturers.

Three general types of malt products are employed by bakers: non-diastatic malt products, medium diastatic malt products, and high diastatic malt products.

Non-diastatic malt syrup is prepared by subjecting the malt extract to the influence of relatively high temperatures which bring about the total inactivation of the amylases and a partial destruction of the proteinases as well. Such a syrup contains maltose, soluble proteins, mineral salts and natural acids which aid fermentation and add flavor, but lacks diastatic activity to convert soluble starches. However, it still possesses a small amount of proteolytic activity useful in dough conditioning.

In diastatic malt syrups the malt enzymes are largely preserved, the relative enzymatic activity being determined by appropriate heat treatment of the malt extract. The amount of diastatic activity is usually expressed in degrees Lintner as determined by the laboratory test for measuring the quantity of sugar produced by the malt when acting on soluble potato starch under standardized temperature, concentration and pH conditions. Low-diastatic malt syrups have in general a Lintner value of less than 30°, medium diastatic syrups have a value of 30°-60°, and high diastatic syrups a value above 70°. It should not be assumed, however, that a malt syrup having a Lintner value of, say, 60° will be twice as effective in a flour dough as a syrup with a Lintner value of 30°, since in a dough we are dealing with a starch that is far more resistant to amylolytic action than is the specially treated soluble potato starch used for the Lintner test. Furthermore, the Lintner test does not measure the proteolytic activity of a malt syrup and syrups having the same Lintner value may vary considerably in the amount of proteolysis they produce in the dough.

The designation of malt syrups according to their diastatic activity is nevertheless useful in that it permits the proper selection of the particular

type of syrup best suited to meet a certain need. Thus if the maximum beneficial effects contributed to the dough and finished product by the constituents of malt syrup are desired, without a need existing for additional diastatic activity, the use of a non-diastatic product would be indicated. For general purposes, however, where a supplementary mellowing agent is required, the use of a medium diastatic malt syrup is preferable. In many instances the flour does not contain a sufficient amount of sugar or is deficient in diastatic activity to meet the requirements of fermentation. In such cases the medium diastatic malt syrup acts to correct these shortcomings by supplying preformed sugar and soluble proteins in addition to diastatic and proteolytic enzymes capable of acting upon the starch and protein substrates of the flour to produce more sugar and contribute to the proper conditioning of the dough.

Because the use of high diastatic malt syrups is difficult to control in the bakery and because slight errors may produce drastic and highly adverse alterations in dough properties, this type of syrup is no longer used extensively. The limited application it still finds in the bakery is largely restricted to certain special products. The same holds true also of malt flour. Since this product is not subjected to mashing and the accompanying starch conversion, its sugar content is relatively low, usually less than 10 percent, while its enzymatic activity is unduly high. Its use in the bakery is therefore not generally recommended unless provisions for strictest control are available.

Brown and Ziegler, (*249*) list the following advantages to be derived from the use of malt syrup:

1. A malt syrup of medium diastatic activity can be used advantageously in amounts of 0.5 percent (based on flour weight) regardless of the diastatic strength of the flour used to supply preformed carbohydrate food, soluble protein and mineral salts to insure vigorous yeast activity.

2. It supplies a balanced enzymatic activity in the dough that assists in the moderate conditioning of the dough and gluten development during the fermentation.

3. It insures the production of maltose during the fermentation from the modified starches present in the flour even after the destruction of yeast activity in the oven, thereby producing more sugar so that the general characteristics and quality of the finished product will be improved, resulting in a loaf of full volume, excellent grain and texture and proper crust color.

4. It aids materially in increasing the moisture retaining properties of the finished product thereby enhancing freshness and keeping quality.

5. One-half percent of malt syrup will compensate partially for the inhibition caused by the use of milk solids in bread that have a tendency to

retard diastatic action and increase the fermentation required to mature a dough containing 6 percent of milk solids.

6. The inclusion of this amount of malt syrup would add only 0.35 percent of fermentable carbohydrate and result in doughs free from buckiness, wildness, or stickiness, without lowered absorption, leaving the remainder to be supplied by some other form of fermentable carbohydrate, such as cane sugar, refined corn sugar or a high conversion corn syrup.

MOLASSES

Molasses, either as a primary product or as a by-product of refined cane sugar production, enjoyed great favor in earlier years as a sweetening agent possessing a characteristic flavor. At the present time, however, its popularity has dwindled considerably, due chiefly to the loss of flavor brought about by modern methods of sugar manufacture. Its use now is largely confined to prepared foods, principally baked goods and confectionery, in which it still performs a useful function as a flavoring agent.

Various commercial grades of molasses are available. Listed in descending order of quality they include (1) "open kettle" molasses, which is reddish yellow in color and contains approximately 70 percent of total sugars and 1-2 percent of ash; (2) first centrifugal or first molasses, a light yellow product of 60-66 percent sugar and 4-5 percent ash contents; (3) second centrifugal or second molasses, which is reddish in color and contains 56-60 percent of total sugars and 5-7 percent ash. Products of lower quality, designated as blackstrap molasses, are not normally included in the edible class and are used chiefly in the manufacture of cattle feed, yeast, alcohol, and numerous other products. They are dark brown in color, have a sugar content of 52-55 percent, an ash content of 9-12 percent, and are characterized by a harsh astringent flavor.

Open kettle molasses, the finest grade, is a primary product obtained by the direct concentration of the juice of sugar cane without removal of any sugar and without the use of artificial clarifying or preservative agents. Evaporation is carried to the point where crystallization sets in. The concentrated juice is then drained off and constitutes the commercial product. If properly aged, it will assume a delicate rum flavor produced by a controlled slight fermentation brought about by certain torulae strains of yeast. Since no bleaching agents are employed in its production, its color is somewhat darker than that of first molasses which has been bleached.

All other types of molasses are essentially by-products of sugar manufacture. Commercial grades are nearly always blended from a great

many batches obtained from single sugar extractions in order to obtain uniform color, flavor and body independent of seasonal variations.

For the sake of completeness mention should also be made of two sweeteners used only to a limited extent in baking and even then only on a regional basis. The first is *sorghum syrup* obtained from the juice of the sugar sorghum, a plant closely related to the sugar cane. Its manufacture is similar to that of sugar cane syrup. The other sweetener is *maple syrup* (and maple sugar). These products are obtained from the sweet sap of certain varieties of the maple tree which are indigenous to the New England section of the United States. Modern methods of manufacture have greatly improved the quality of maple products, both with respect to their flavor and their wholesomeness.

CHAPTER XI

PLASTIC BAKING FATS

Introduction. Prior to the development of a highly specialized shortening industry, the principal animal fat used for edible purposes was lard, the body fat of hogs. Two attributes of lard ensured for it this position of preeminence. One was its characteristic flavor which found a greater general acceptance than that of any other generally available animal fat. The other, and probably more important attribute, was its consistency which at room temperature was nearly ideal for the proper incorporation of the fat into pie crusts, cakes, pastries and bread. Neither beef or mutton tallow, nor marine oils, approached lard in this respect, the former being too firm, the latter too fluid. Furthermore, these other animal fats also possessed less acceptable flavors.

Lard, however, was handicapped by the fact that it was a by-product, rather than a primary product of the meat-packing industry. This meant that the supply of lard was never directly related to the demand for it but rather to the demand for pork. Also, as the use of plastic shortening agents expanded, the production of lard fell far short of the requirements. This chronic shortage of lard led to attempts to convert liquid vegetable oils into plastic shorteners. At first this was accomplished by blending relatively large proportions of vegetable oils, principally refined and deodorized cottonseed oil, with relatively small amounts of oleostearine or other very hard animal fats to yield a plastic product which simulated lard in its consistency. One of the first formulas used for this purpose called for 80 percent cottonseed oil and 20 percent oleostearine. These new shortenings were called "lard compounds" or blended shortenings and were designed as lard substitutes. In general they possessed a satisfactory flavor, consistency and keeping quality and were less expensive than lard (*250*).

With the introduction of catalytic hydrogenation in about 1910, the first all-vegetable shortenings made their appearance as baking fats. Vegetable oils could now be completely hardened by means of the hydrogenation process and blended with liquid vegetable oils to the desired consistency. The shortening manufacturers thus became independent of the meat-packing industry which had previously entered the shortening field and continued to produce blended shortenings. By improving refining, bleaching, deodorization and solidifying methods, all-vegetable

shortenings were soon able to maintain themselves on their own merits and to overcome their previous status as lard substitutes. Shortening manufacturers next adopted the practice of hydrogenating the entire mass of vegetable oil to the desired consistency. While this was merely another approach to the problem of obtaining the proper balance between saturated and unsaturated glycerides to produce a liquid-solid glyceride blend of the proper plastic character, it also resulted in a product which had a much lower iodine value than did blended shortenings and which therefore was much more resistant to atmospheric oxidation or rancidity development. The all-hydrogenated shortening found great favor with cake bakers because of its neutrality, stability and uniformity. At present all shortening manufacturers produce this variety, including the meat packers, although the latter also make available improved blended shortenings having a wider plastic range than the all-hydrogenated type (*250*).

In analyzing the respective suitabilities for baking purposes of lard and vegetable shortenings, Bailey makes the following observations (*16*):

"The high degree of favor enjoyed at present by the vegetable shortenings is doubtless due in part to their superior physical properties, as compared with lard. Much American lard is not only rather softer in consistency than is desirable, but is also nonuniform in consistency, due to variations in composition according to the feed of the hogs, and other factors. Also, lard does not cream well in the manufacture of cakes and sweet goods, and is much less resistant to deterioration through oxidation than good vegetable shortening. Good creaming and mixing properties, high stability, and uniformity, are properties which are particularly desired by commercial bakers. . . . Another property of lard which now appears to be rather more of a liability than an asset is its distinctive flavor. Through prolonged use of odorless and tasteless shortenings and cooking oils, a large and apparently growing segment of the American people has developed a distaste for all natural fat flavors save that of butter."

The great emphasis placed upon plasticity in bakery shortenings derives from the important role which this property plays in determining the character of the baked goods. Plastic fats, when mixed into a batter or dough, are extended into streaks and films which lubricate large surfaces in the dough and thereby produce a maximum shortening effect for a given quantity of fat. Plastic fats are further able, during the mixing or creaming process, to entrap and retain considerable quantities of air. This produces an important leavening effect, particularly in cakes of high sugar content. Liquid oils, on the other hand, are dispersed upon mixing throughout the dough in the form of minute globules which are far less effective in their shortening and aerating actions than are fat films.

LARD

The annual production of lard in the United States has ranged between 2 and 2.5 billion pounds during the past quarter century, with the exception of a period of four years beginning with 1935 when government control restricted production. A considerable proportion of this volume is consigned to commercial bakeries for use as a shortening agent.

Lard is processed variously to produce different varieties known as "prime steam lard," "kettle-rendered lard," "leaf lard," etc. By far the greater amount of lard is wet-rendered in closed vessels under steam pressure to yield *prime steam lard*. The commercial refined lard is prime steam lard which has been dried, clarified and solidified, and packaged in drums, tubs, cans, pails and cartons for marketing. Lard of similar quality and used for the same general purposes is also obtained by a dry rendering process or open kettle process. Dry-rendered lard can be distinguished from prime steam lard by its noticeable cooked flavor and slightly darker color imparted to it by traces of protein materials. *Leaf lard*, which is markedly firmer in consistency than ordinary prime steam lard, refers specifically to lard obtained by the open kettle process from the internal "leaf fat" of hogs. Because of its distinctive flavor it is little used in commercial baking and is principally designed for household cookery. *Neutral lard*, a wet-rendered product from selected fats and possessing a very mild flavor, was formerly produced in considerable quantities for margarine production. At present it constitutes only a minor and relatively unimportant fraction of total lard production. Lard, to be marketed as such, must conform to the following definition established by the Bureau of Animal Industry of the Department of Agriculture:

"Lard, the fat rendered from fresh, clean, sound fatty tissues from hogs in good health at the time of slaughter, with or without lard stearine or hardened lard. The tissues do not include bones, detached skin, head fat, ears, tails, organs, windpipes, large blood vessels, scrap fat, skimmings, settling, pressings and the like, and are reasonably free from muscle tissue and blood."

Lards may vary considerably in their composition and characteristics, depending upon the type of feed received by the animal, its age at slaughter and the part of the carcass from which they are rendered. As a general rule, lards obtained from hogs fed a ration high in fat content, that is, a ration consisting of fair proportions of soybeans or peanuts, are characterized by a high iodine value and a correspondingly high degree of softness. On the other hand, high protein fat-free rations result in lards of lower iodine value and firmer consistency. Age of animal at time

of slaughter has also been shown to affect lard consistency, the older animals yielding lards of a firmer body. The part of the carcass from which the fat is rendered also exerts a pronounced effect upon lard consistency. As a general rule, lard obtained from internal organs is comparatively firm, an example being leaf lard, while the exterior fatty tissues yield lard of higher iodine value and a correspondingly softer texture.

These variations in lard composition and characteristics require the application of exacting control measures at the rendering plants to ensure a product possessing a fair degree of uniformity. Generally it is possible for packing plants to blend lards of varying consistencies in such proportions that the proper degree of plasticity is obtained in the commercial product. Excessively soft lards are commonly stiffened by the addition of a small proportion of hydrogenated lard stearine, which is prepared by deodorizing refined lard and then hydrogenating it.

In an attempt to approach the neutrality and other desirable properties of vegetable shortenings in lard products, a type of hydrogenated and deodorized lard was introduced in about 1929. In the processing of this product, the original soft lard is subjected to much the same type of refining, bleaching, hydrogenating and deodorizing treatments required by vegetable oils. Hydrogenated lard is different from ordinary commercial prime steam lard by being flavor- and odorless, more stable, of a whiter color, and by possessing a more uniform consistency and improved baking quality. A lard of comparable quality is also produced by similar processing except that instead of hydrogenation, the consistency of the lard is adjusted by the addition of a suitable proportion of hydrogenated lard stearine.

A serious problem which has confronted meat packers and which is still only partially solved is the relatively poor keeping quality of lard, especially when compared with vegetable shortenings. Lard, in common with animal fats as a group, is almost completely devoid of natural antioxidants to which vegetable fats largely owe their high stability. While improvements and greater care in processing have resulted in imparting a somewhat better keeping quality to lard, the real solution appears to lie in the use of antioxidants. The effectiveness of various substances possessing antioxygenic properties has been briefly indicated in the chapter on FATS AND OILS.

SHORTENINGS

Raw Materials. Shortenings may be of two general types which possess fairly clear-cut differences in their characteristics, namely compound shortenings and all-hydrogenated shortenings. Compounded short-

enings are further differentiated into those which consist of animal fats blended with vegetable oils, and those which consist exclusively of vegetable oils, part of which have been hydrogenated. All-hydrogenated shortenings are also differentiated into general purpose shortenings, biscuit and cracker type shortenings, and high emulsifying shortenings.

Since a suitable consistency may be imparted to shortening either by hydrogenation or the admixture of naturally hard or artificially hardened fats, the original consistency of vegetable fats is of little significance. As a consequence a wide variety of oils may be used in the manufacture of shortenings.

Animal fats used in the production of compound shortenings are oleostearine, edible tallow and lard. Oleostearine, which is a firm fat, generally constitutes some 20 percent of compound shortenings, the remainder being made up of liquid vegetable oils. Tallow, obtained from mutton or beef, was formerly used to the extent of 50 percent in compounds. At present it may range from 25 to 40 percent, additional stiffening of the shortening being obtained either by hydrogenation or the addition of hardened vegetable stearines. Compound shortenings usually also contain some rendered pork fat, which is obtained from certain fatty hog tissues which cannot be utilized in lard rendering. In times of depressed lard prices, lard itself may be incorporated in compound shortenings.

Other animal fats utilized in compound shortening include fish and whale oils. Both of these fats are extensively hydrogenated prior to their use in order to reduce their degree of unsaturation and their tendency toward flavor reversion. Fish oils, as a general rule, are used only in lower grade products.

Among the principal vegetable oils used in shortening production are cottonseed, peanut, soybean, corn, coconut and palm oil. The varying consumption of these as well as of less important vegetable oils and of animal fats in the manufacture of shortenings in the United States in recent years is shown in Table 84.

Of the principal vegetable oils indicated above, soybean oil is the only one whose use is limited by its tendency to revert in flavor. Cottonseed and peanut oils may be used interchangeably and either of them may constitute a major proportion of this type of shortening. Palm oil, intended for use in compounded shortenings, may require hydrogenation to improve its naturally dark color. Coconut oil is characterized by a short plastic range and low smoke point and is used only sparingly for these reasons.

Compounded Shortenings. As pointed out above, compounded shortenings may be either blends of both animal and vegetable fats or consist

only of vegetable oils part of which have been hydrogenated. The former are now made almost exclusively by the meat-packing companies since they are the primary producers of the necessary animal fats, oleostearine, lard and tallow. Compounded shortenings containing animal and vegetable fats are at present nearly evenly divided between those in which oleostearine is used to obtain the desired consistency and those in which tallow performs the stiffening function. Oleostearine compounds usually contain some 20 percent of the hard animal fat and 80 percent cottonseed or peanut oil. The tallow compounds contain on an average some 35 per-

TABLE 84.	OILS AND FATS CONSUMED IN MILLION POUNDS IN THE MANUFACTURE OF SHORTENINGS IN THE U. S. IN RECENT YEARS

Oil or fat	1943	1944	1945
Cottonseed oil	572	490	487
Soybean oil	568	620	683
Palm oil	1	0	0
Peanut oil	51	61	51
Coconut oil	0	1	0
Corn oil	6	5	2
Linseed oil	7	0	0
Oleostearine	30	22	24
Edible tallow	79	60	79
Lard and rendered pork fat	36	39	23
Fish oils	13	3	3
Other oils	7	8	23
Total	1,370	1,309	1,375

cent of the animal fat and 65 percent vegetable oil. Since a simple mixture in these proportions yields a product which is too soft in consistency, additional stiffening is obtained either by slight hydrogenation or by the substitution of about 5 percent of the liquid oil with hydrogenated vegetable stearine. Compounded shortenings containing lard or rendered pork fat often contain 80 percent or more of these fats with the balance composed of hydrogenated oils.

All-vegetable compound shortenings closely approximate the animal and vegetable compounds except that in their case the hard animal fats are substituted by highly hydrogenated vegetable oils. The content of hardened vegetable oil in these compounds lies generally within the range of 10 to 15 percent, although with specific products it may both exceed or fall short of these limits. A flavor- and odorless compound is obtained with 10 percent vegetable stearine and 90 percent cottonseed oil (16).

Except when these all-vegetable compounds are well refined and thoroughly deodorized they are inferior to all-hydrogenated shortenings and consequently sell at a somewhat lower price.

All-Hydrogenated Shortenings. All-hydrogenated shortenings constitute one of the major types of fat used in commercial cake and cookie production. They are also used to varying degrees in the majority of other bakery products. They are characterized by neutrality in flavor and odor, exceptional keeping quality, long plastic range, and good creaming qualities. The principal oils used in their manufacture are cottonseed, soybean and peanut oils. All-hydrogenated shortenings sometimes contain animal fats, the most common of which is lard. They differ from the compounds in that in their manufacture the entire product is hydrogenated to the desired consistency, the process being closely controlled so as to bring about a major reduction of linoleic acid to oleic acid. Linoleic acid contains two double bonds and is therefore quite susceptible to oxidation, whereas the more stable oleic acid has only one double bond. At the same time the reduction to any marked extent of oleic acid to stearic acid is undesirable because the latter has a relatively high melting point and may lead to excessive firmness in the final product. These aspects of hydrogenation will be discussed more fully in a subsequent paragraph. All-hydrogenated shortenings may be made from a single oil, such as cottonseed oil, or they may contain several oils, such as peanut, soybean, sesame and other oils. The shortening's stability depends to some extent upon the original oil used, peanut and soybean oils being more stable than cottonseed oil when hydrogenated to the normal shortening consistency, although soybean oil tends to revert in flavor and should not therefore be used extensively in high-grade products. Pure cottonseed shortening has a normal keeping time of 70 to 80 hours as measured by the Swift method, whereas shortenings prepared from peanut and soybean oils have keeping times of 100 to 200 hours. These values compare with about 8 to 10 hours for plain lard, about 25 for deodorized and hydrogenated lard, 12 to 20 for animal and vegetable compounds, and 15 to 28 for all-vegetable compounds (*16*). The use of antioxidants has increased the Swift keeping time of products containing lard to 40 hours for stabilized plain lard, 50-75 hours for stabilized, refined and deodorized lard, and to 75 hours and higher for stabilized, hydrogenated lards.

So-called high emulsifying or "high ratio" (the term "high ratio" is copyrighted by Procter and Gamble Co.) shortenings were introduced about 1933. They are distinguished from ordinary all-hydrogenated shortenings primarily by their greater proportion of mono- and diglycerides which account for the remarkable improvements in the emulsifying

properties of the newer shortenings. Because of the far greater dispersion of the fat in doughs and batters obtained with these shortenings, and the resultant improvement in batter strength, especially in the presence of high sugar contents, these high emulsifying shortenings have found their major application in commercial cake production.

Manufacturing Process. The natural vegetable oils, obtained from seeds or fruits by pressing or solvent extraction, contain extraneous matter in varying concentrations. These include free fatty acids, natural coloring materials such as chlorophyll and carotene, oil soluble vitamins such as A, E and K, and natural antioxidants. Some protein material, phospholipids, gums, resins, etc., derived from the seed are also carried through into the extracted or expressed oil (*251*). The object of the refining process is to obtain as complete a removal of the undesirable impurities as possible, without, however, eliminating such desirable compounds as the vitamins and antioxidants. In refining, the raw oil is first treated with an alkali which, by combining with the free fatty acids, forms a soft soap. The soap particles, on settling, serve as an adsorbing medium which carries down with it the various impurities, resulting in a clean, light-colored and practically neutral oil. Generally a further bleaching of the color is required, if the oil is to produce a high-grade shortening. This is accomplished by heating and treating the oil with a small amount of diatomaceous earth, followed by thorough filtration.

The purified oil is then ready for hydrogenation. This process may be applied either to the entire oil if an all-hydrogenated shortening is desired, or to only a part of the oil if a compounded type is to be produced. In hydrogenation, the oil is treated with purified hydrogen gas under pressure in the presence of a catalyst, which is usually in the form of active nickel associated with a finely divided carrier. The reaction of hydrogen with unsaturated glycerides is aided by heating and agitation, and is terminated when the fat has attained the proper degree of unsaturation. An attempt is made to obtain selective hydrogenation, that is, the reduction of the more unsaturated acids to less unsaturated acids, avoiding at the same time the creation of the so-called iso-oleic and iso-linoleic acids which have relatively high melting temperatures and therefore tend to impart excessive hardness to the shortening. In most cases it has been found that as the selectivity of the reaction improves with respect to the hydrogenation of the more unsaturated fatty acids, the amount of iso-oleic acids tends to increase. It also appears that the more unsaturated the original oil, the more iso-acids are formed during its hydrogenation to any predetermined degree. In actual practice these factors limit the extent to which a particular vegetable oil may be hydrogenated to produce a fat having suitable plastic properties (*251*).

Aside from imparting the desired consistency to a fat, hydrogenation is of importance also in that it greatly improves the stability of the fat by reducing the degree of unsaturation. Stability is further augmented by the natural presence of certain antioxidants in vegetable oils, notably the tocopherols and vitamin K. The tocopherols are present in cottonseed oil and both tocopherols and vitamin K occur in soybean oil. By careful processing a large part of the antioxidants present originally in the crude oils persists through processing and remains in the final product. While each of these antioxidants is highly effective alone, they exhibit a synergistic effect which greatly increases their combined stabilizing action. Properly hydrogenated soybean oil has an unusual stability on this account and is frequently added to cottonseed oil to improve the latter's keeping quality.

After the oil has been hydrogenated to the desired consistency it is subjected to a deodorizing treatment which consists of blowing it with superheated steam under a high vacuum. This treatment removes all volatile aromatic substances, such as free fatty acids, aldehydes, etc., leaving the final product bland and neutral in flavor. The oil is then solidified by chilling and passed through texturating valves which impart to it a smooth consistency. The product is then ready for packaging. The commercial packages usually used for this purpose are 50 and 100 lb. capacity tins and steel drums having a capacity of 400 lbs.

BUTTER

Butter is used in baking principally for the distinctive flavor it imparts to baked products. This flavor is unique with butterfat and it has as yet proved technologically impossible to duplicate it exactly in any other fat product. Despite the fact that butter lacks some important characteristics of other plastic shortening agents, such as uniformity from one batch to the next, a long plastic range, and keeping quality at normal temperatures, its superiority of flavor when fresh is such that it continues to be used in large amounts in commercial baking, especially in the production of high grade specialty sweet goods and cakes.

Butter is legally defined as follows:

"Butter. The food product usually known as butter and which is made exclusively from milk or cream, or both, with or without common salt, and with or without additional coloring matter, and contains not less than 80 percent by weight of milk fat, all tolerances allowed for."

Although butter, as obtained from creameries, is relatively constant in composition, especially as far as its fat content is concerned, it is subject to considerable variations with respect to its consistency and flavor, depending upon seasonal variations in feed and upon the animals.

The method of manufacture, i.e., whether it is made from sweet or ripened cream and whether it is salted or unsalted, also determines to a marked degree the general characteristics of the product. Seasonal effects are also observed with regard to the product's color and vitamin A and D contents. It is thus common practice to add artificial coloring to the cream to maintain a consistent yellow hue in creamery butter.

A chemical analysis of butter is usually given in terms of the percentages of fat, water, salt and casein present. The average composition of butter, based upon published analyses of more than 12,000 samples, is as follows: Fat, 80.47 percent, moisture, 16.34 percent, salt, 2.35 percent, curd or casein, which includes the protein, mineral substances and lactose derived from the buttermilk retained by the butter, 0.84 percent *(252)*. Butter also usually contains about 0.2 percent of phosphatides, calculated as lecithin, and incorporated air which usually amounts to 1 to 5 percent by volume *(16)*.

The characteristic flavor and aroma of fresh butter, which distinguish it from all other edible fats, may show a considerable variation between different lots of butter. The flavor depends to a large extent upon the quality of the cream used in its manufacture, the method of processing, and the manner and length of butter storage. Butter is extremely sensitive to flavor taints and will absorb most odors to which it is exposed for even short periods.

The flavor of butter was formerly attributed to butyric and lactic acids, the former being a natural constituent of the butterfat glycerides and the latter being formed by the fermentation of lactose, the milk sugar. While these substances undoubtedly contribute in a minor way to the formation of the distinctive flavor of butter, more recent investigations have shown that it is derived primarily from a very small amount of a compound known as diacetyl. Diacetyl is by no means limited in distribution only to butter but occurs in other foods and aromatic products, including freshly baked bread. It is formed by the fermentation of citrates present in milk by means of certain strains of lactic acid bacteria. Diacetyl occurs in butter in extremely small quantities, ranging from 0.1 p.p.m. in low flavored butter to 2.0 p.p.m. in highly flavored butter.

While butter stored at very low temperatures will not deteriorate for several months, it generally will undergo bacterial spoilage rather rapidly when kept at room temperature. This type of spoilage differs from that of lard and vegetable shortenings in that it is induced by bacterial or mold agents rather than by oxidation. While oxidative deterioration, imparting to butter a tallowy flavor, does occur, it is rather rare. Since bacterial and mold growth occurs in the aqueous phase representing the

moisture content of butter, the inclusion of 2.5 to 3 parts of salt to 15 parts of water is partly designed to retard this growth and thereby prolong the storage life of butter. Butter is scored largely on its flavor so that freedom from off-flavors, whether these are brought about by bacterial action or contamination by environmental conditions, is of utmost importance.

Since butter is used in baking primarily for the flavor it imparts to baked goods, the mildly flavored table butters are found less suitable for this purpose than the more strongly flavored butters, commonly known as cake butters. In baking practice, butter may be used in the batter or dough as part of the shortening, it may be incorporated into the icings used on cakes and sweet goods, or it may be melted and brushed onto the baked products.

MARGARINE

Margarine was developed as a substitute for butter by the French chemist Mege-Mouries during the Franco-Prussian War (1870–71). While its acceptance was at first retarded by the generally low quality of the product, its consumption since the turn of the century has increased steadily until in some European countries the per capita use exceeds 20 pounds annually. Current per capita consumption of margarine in the United States, where its manufacture and sale has been subjected to considerable legislative restrictions, is about 2.5 to 3.0 pounds per year.

Margarine was originally produced exclusively from oleo oil prepared by the fractional crystallization of beef fat, and milk, the resulting product being called oleomargarine. Later neutral lard in carefully adjusted proportions was used to supplement the oleo oil. With improvements in the refining, hydrogenation and deodorization of vegetable oils, cottonseed and soybean oils began to replace the two animal fats until at present most of the high grade margarines produced in the United States are products containing only hydrogenated vegetable oils. Thus the combined animal fats (oleo oil, neutral lard, oleostearine and other fats) used in margarine production in the United States in 1942 amounted to 37.6 million pounds, compared to 166 million pounds of cottonseed oil and 133 million pounds of soybean oil for the same year. The preference for hydrogenated vegetable oils for the manufacture of margarine is based on their greater stability, neutrality of flavor and uniformity of consistency. The recently permitted addition of vitamin A to margarine in amounts equivalent to its normal content in butter has placed the manufactured product on a practical par with butter as far as nutritive value is concerned. In fact, some of the better margarines re-

semble butter so closely in their flavor, consistency and other characteristics that the consumer finds it difficult to distinguish the one from the other.

In margarine production the fats are first adjusted to the suitable consistency and then mixed into an emulsion with milk which has previously been ripened with a selected bacterial culture to impart to it a butter flavor. Generally lecithin or some other surface active agent, such as monoglyceride, is added to improve the emulsifying properties of the margarine. The mixture is then solidified, worked with 2.5 to 3.0 percent of salt and kneaded into a homogeneous mass, which is then packaged for marketing.

Margarine finds specialized application in the production of puff pastry. The margarine, or puff-paste fat, used for this purpose is specially compounded, consisting usually of about 35 percent of oleostearine and 65 percent of deodorized cottonseed oil, the fat mixture being emulsified with 6 to 8 percent of milk. Vegetable oil hydrogenated to the consistency of oleostearine may replace the animal fat if desired. The final product is characterized by a melting point in excess of 118° F. and possesses a rather tough and highly extensible body which renders the fat particularly suitable for the "rolling in" process employed in the production of puff pastry.

FRYING FATS

The commercial production of deep fried goods, such as doughnuts and similar types of fried cakes, has in recent years experienced a tremendous expansion until at present a so-called doughnut department constitutes a regular branch of many commercial baking plants. This phenomenal growth is due partly to the aggressive merchandising by the suppliers of frying equipment and materials, and partly to the far-reaching mechanization of the frying operations which, in the more modern plants, are nearly completely automatic.

Since the functions of fat in deep frying differ markedly from those of the shortenings incorporated in the dough or batter, it is only natural that the properties sought in the frying fats should also differ from the characteristics required of ordinary shortenings. Thus whereas uniformity and plasticity are of great importance in shortenings, they are of less significance in frying fats. On the other hand, frying fats are exposed to the hydrolyzing effect of high temperatures for long periods of time, while this is not the case with regular shortening. Thus such properties as high smoke point and resistance to rapid hydrolysis and polymerization are of primary importance. In general, frying fats to be satisfactory must meet the following requirements: (1) Permit the normal structural

development of the doughnut or other type of fried cake as it passes through the frying medium; (2) impart no undesirable flavors to the products during frying and after they have been packaged; (3) the absorbed fat must congeal sufficiently during cooling of the product so as to prevent discoloration and subsequent "oiling" of the sugarwhite; and (4) continuous frying at 365° F. to 375° F., where constant replacement of the fat absorbed by the fried cakes is practiced, should not result in radical changes of the fat's performance. Volume, fat absorption, inner structure and crust characteristics of the doughnuts or fried products should remain normal (*253, 254*).

A number of extensive deep frying tests, involving the use of commercial doughnut machines, have been reported. Thus Lantz and Carlin (*255*) have investigated the suitability of five different shortenings for deep frying. Three of the shortenings were of the all-hydrogenated variety, while two were of the compound type. They found that compound type shortenings about equalled the all-hydrogenated shortenings in general performance. More recently Arenson and Heyl (*256*) reported on the effects of various vegetable shortenings on doughnut quality. Four types of shortenings, varying exceedingly in degree of saturation, were selected. These included (a) a refined, bleached, deodorized corn oil with a Peroxide Value (PV) of 1.6, a Free Fatty Acid content (FFA) of 0.02 percent, and Active Oxygen Hours (AOH) value of 12; (b) the same corn oil plus 15 percent peanut stearine, with a PV—1.0, FFA—0.01, AOH—12; (c) a partially hydrogenated all cottonseed shortening containing free oil and stearine, with a PV—1.0, FFA—0.04, AOH—45; (d) an all hydrogenated cottonseed shortening, with a PV—4.0, FFA—0.02, AOH—125. In discussing the results obtained, these writers point out that neither the peroxide values of the original fats nor their active oxygen hour ratings before and during their use are of positive value in judging the frying quality of a shortening for doughnuts. Thus while there was a marked decrease in the active oxygen hour ratings on all of the shortenings after they had been subjected to frying conditions for one-half hour, this did not lead to early oxidation of the fat absorbed by the doughnuts. They observed that approximately 3 grams of fat were absorbed by each doughnut for each type of shortening tested, which indicates that neither the degree of saturation of the shortening nor its free fatty acid content (over a range of 0.6 percent) has an effect upon fat absorption. It was also found that there occurs a definite steady rise in free fatty acid content in all of the shortenings during the frying period.

It is a common experience in deep frying that fresh shortenings fail to yield high quality doughnuts during an initial frying period which varies in length with different fats. The point in usage at which the shortening

functions properly to yield normally shaped doughnuts is called the quality period and appears to be correlated with an increase in free fatty acid content in the shortening. In general, the greater the saturation of the fat used for deep frying, the more protracted is the pre-quality period. Arenson and Heyl (*256*) found in the case of the fully hydrogenated cottonseed shortening that a free fatty acid content of 0.35 percent was reached before quality doughnuts resulted. Unhydrogenated corn oil, on the other hand, reached the quality period when its free fatty acid content was only 0.1 percent. Since in commercial frying, fresh shortening must constantly be added to the frying medium to replace the absorbed fat, a reduction of the pre-quality period is of obvious importance, especially when it is remembered that the replacement period averages less than ten hours in frying units that produce from 400 to 600 dozen doughnuts per hour. It has been found that when fatty acids prepared from partially hydrogenated cottonseed shortening were added to the same type of shortening in amounts calculated to produce a fatty acid content of 0.5 percent, the pre-quality period was almost completely eliminated.

FUNCTIONS OF FATS IN BAKING

The importance of fat as a baking ingredient varies markedly in accordance with the type of bakery product. In certain types of cakes, such as the sponge cakes, shortening is not used at all. In some yeast-raised products, notably bread and similar items, the inclusion of fat is more or less optional. Here its contribution to the product characteristics is of relatively minor significance, although it does exert a beneficial effect upon quality. Other types of cakes, including white, yellow, pound and other cakes, as well as such products as pie crust, certain pastries and cookies, require a considerable proportion of shortening for the development of their characteristic structure.

Keeping in mind this variability in the importance of fat as a baking ingredient, the various functions of shortening in baked products may very generally be listed as follows: (1) to produce shortness and tenderness, (2) to aid in the aeration of the product, (3) to improve the eating quality of the product, (4) to stabilize cake batters, and (5) to improve the keeping quality of the product. To these functions may be added, in the case of butter, the contribution of a distinctive flavor, and in the case of all types of shortenings, the improvement in the nutritive value of products containing added fats.

Shortening Function of Fats. Originally fats were used in baking principally for the tenderness or shortness they impart to chemically-leavened baked products. This function is still of primary importance in such products as biscuits, wafers and cookies, and continues to be of

utmost significance in all types of cakes in which shortening is used to any considerable extent. This shortening effect is due partly to the chemical nature of fat and partly to its plastic character. Fat is the only major ingredient in the cake batter which does not undergo drastic changes during baking. Cake batters consist of mixtures of certain dry or nonaqueous ingredients and of watery or liquid ingredients. The dry ingredients include flour, sugar, salt, baking powder, fat, etc., while the two major liquid ingredients are egg and milk. When mixing occurs, the sugar, salt, and baking powder dissolve in the liquid ingredients to form a solution which freely wets the flour particles to form a coherent mass. No such intimate mixture, however, occurs with fat which is dispersed throughout the batter in the form of small, irregularly shaped particles. The resultant films of fat break the continuity of the batter's gluten and starch structure, thereby weakening it and preventing the formation of a hard and tough mass. The plastic character of the shortening assures its dispersion in the form of films or clumps rather than of globules, as is the case with oil, and thus creates a much larger fat surface than is possible with liquid oils. The practical absence of a shortening effect in liquid oils is generally attributed to their lack of plasticity.

While several studies on the distribution of fat in cake batters have been reported (*257, 258, 259*), the most clearly defined results have been obtained by Carlin (*260*). By following the behavior of fats in cake batters under a microscope and recording these observations by means of photomicrographs, Carlin showed that in white cake batter the fat is dispersed as a discontinuous phase in the form of irregular clumps or "lakes" (see Figure 43), while the continuous aqueous phase is comprised of the dissolved sugar, salt and baking powder and the suspended flour and eggs. The addition of emulsifying agents (monoglycerides) resulted in a clearly perceptible increase in the degree of dispersion of the fat. This increased dispersion was characterized by both a greater number of fat particles per unit area and a decrease in the size of the individual fat particles. With each addition of emulsifying agent, up to the level of 5 to 6 percent based on the quantity of fat used, there was a corresponding increase in the volume of the cake obtained. Too fine a dispersion of the fat in the cake batter, such as was produced by the inclusion of 8 to 9 percent of emulsifying agent, resulted in a decline of cake volume, indicating that there is a limit to which fat dispersion may be carried.

The shortening value of a fat may be determined by means of a "shortometer," a device developed by C. E. Davis (*261*) and subsequently improved by Bailey (*262*). This instrument measures the breaking strength of standard wafers baked with the shortening under investiga-

tion.   While this test gives a fairly accurate indication of the relative shortening values of different fats, it is subject to marked variability in the hands of different operators.   In general, the shortening value of a fat appears to be related to its plasticity, the softer fats, such as prime steam lard, being superior in shortening power to the harder fats.

Aerating Function of Fats.   In the production of certain cakes, notably yellow and white layer cakes and pound cakes, shortenings play a decisive role in determining the structural characteristics of the products
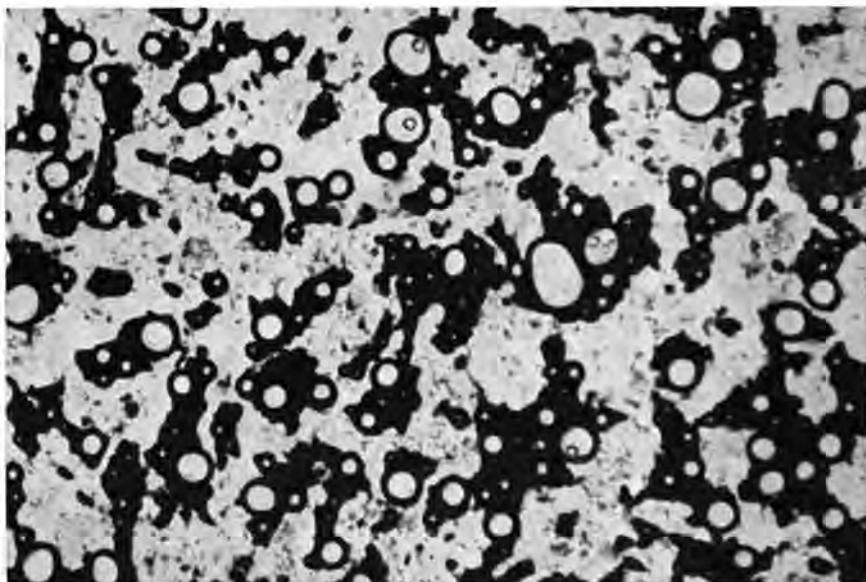

FIG. 43—Microphotograph of white layer cake batter showing the dispersed form of shortening. The fat has been stained dark. (*Courtesy Swift and Co.*)

as developed by leavening.   Even though chemical leavening agents, which on heating generate carbon dioxide gas and thereby aerate the baking batter, are used in such cakes, they require considerable incorporation of air during the mixing process if proper volume, grain and texture are to result.   The incorporation of the air during creaming is solely a function of the shortening, for it is the fat that entraps the air in the form of tiny cells or bubbles.   Carlin (*260*) has confirmed the observations of several previous investigators by showing microphotographically that the creamed-in air is confined only to the fat phase of the cake batter and that no air cells are present in the aqueous phase.   These air cells or bubbles form nuclei for the accumulation of water vapor generated by the baking heat as well as of the carbon dioxide released by the chemical leavening agents, resulting in their expansion and a corresponding in-

crease in the dough volume. Carlin has observed that as the heat of baking melted the fat confining the air bubbles, they were released into the aqueous medium where they began to coalesce, the larger bubbles absorbing the smaller ones. As the end of the baking process approached, a sudden increase in internal pressure was observed, and the air cells appeared to explode. Significantly enough, the same investigator also found that upon the release of carbon dioxide from baking powder few, if any, new gas cells are formed, the carbon dioxide gas collecting at the
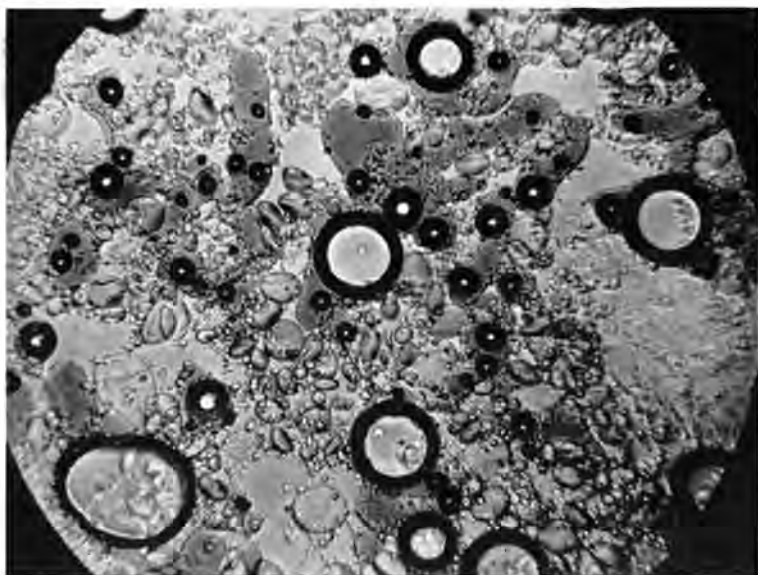

Fig. 44—A microphotograph of cake batter, in which the fat has been stained dark, shows that air cells are restricted to fat masses. (*Courtesy Procter & Gamble Co.*)

air space interface and increasing the volume of each pre-existing air cell. This observation underscores the great significance of the mixing operation in which a maximum incorporation of air and dispersion of fat should be aimed at for optimum cake volume.

It will be found that when cake batters incorporating different amounts of air are prepared, the doughs containing large amounts of air entrapped in the fat will yield cakes of larger volume than will batters containing relatively little air. Also, the more complete the dispersion of the entrapped air, which presupposes a correspondingly complete dispersion of the fat, the finer will be the grain and texture of the finished cake.

The leavening action of the fat-entrapped air in cakes containing no chemical leaveners is far greater than can be expected solely on the basis of the thermal expansion of the air during baking. The pronounced ex-

pansion in cake volume on baking must therefore be attributed to the greatly increased water vapor pressure within the air cells at high temperatures. Water vapor, however, cannot exert a leavening action without the pre-existing air bubbles as was demonstrated by Dunn and White (*263*) who showed that pound cake batters completely devoid of air did not rise at all in the oven, though the water vapor pressure developed in them by the baking temperature must have been of the same order as that in aerated batters. The air cells in the fat are necessary to act as nuclei in which the water vapor can accumulate and expand. The relationship between the leavening action attributable to the thermal expansion of the incorporated air and to the increased water vapor pressure in a pound cake formula containing no chemical leavening agent is summarized by Bailey (*16*) as shown in the following table.

TABLE 85.   TYPICAL EFFECT OF INCORPORATING AIR IN A POUND CAKE FORMULA CONTAINING 21 PERCENT FAT AND NO CHEMICAL LEAVENING AGENT

Experiment	A	B
Air incorporation in shortening	Low	High
Calculated volume of dough without air, cc	377	377
Actual volume of dough, including air incorporated, cc	543	662
Volume of air in dough, cc	166	285
Volume of cake, cc	1,140	1,520
Expansion of dough during baking, cc	597	858
Calculated expansion of air due to heating in oven (70-212° F.), cc	42	71
Percentage of total expansion due to thermal expansion of air	7.0	8.3
Percentage of total expansion due to increased vapor pressure of water	93.0	91.7

The ability of fat to absorb air during mixing is called its creaming quality. Since the role of fat-entrapped air is a primary factor in determining cake quality, it is evident that the creaming quality of a fat largely governs its suitability as a cake shortener. Although it is possible to compensate a deficiency in air absorption of a fat by means of baking powder or other chemical leavener and thereby obtain a cake of satisfactory volume, the cake's grain will be coarse and marked by large pockets since the action of the baking powder will be uncontrolled by the air. It is therefore of considerable importance for the baker to be able to test the creaming qualities of a shortening and evaluate its suitability.

A rational method for the evaluation of the creaming qualities of shortenings has been suggested by Bailey and McKinney (*264*), in which creaming is expressed as the percentage of air incorporated by the shortening on the basis of its own volume. The test is carried out by mixing together in a small machine a quantity of shortening and granulated

sugar, in definite proportions and amounts, and determining the density of the mix at intervals during a prolonged mixing period. From the densities obtained the percentage of air incorporated is calculated from a given formula. Sometimes eggs are also included in the mixture. Usually the densities of the finished batters of test cakes are also determined and correlated with the finished cake volumes.

Using this method for the purpose of following the incorporation of air through the various steps of mixing a cake, the authors describe the results of a test with two different shortenings, A and B, not otherwise identified, which were used to make pound cakes according to the following formula:

Shortening	88	parts
Sugar	100	"
Eggs	112	"
Milk	12	"
Flour	100	"

The blending of the various ingredients was carried out as follows:

Mixing Period	Minutes	Operation
1	5	Sugar and shortening creamed
2	5	Eggs gradually added
3	5	Mixing continued
4	3	Milk and flour added

With shortening A, the air content increased smoothly up to the point where the milk and flour were added, being some 175 percent during the first period, 270 percent during the second period, 300 percent during the third period and declining to 275 during the fourth period. Shortening B incorporated some 210 percent of air during the first period, but not only failed to gain additional air after the eggs were added, but actually lost some 40 percent, its final air content being some 125 percent. The finished cakes showed a correspondingly marked difference in volume. The authors have examined a large variety of shortenings by this method and have arrived at the following generalizations. Good shortenings will incorporate a maximum of about 270 percent air when creamed with granulated sugar at the optimum ratio of about two parts of shortening to three parts of sugar, by weight. In practical cake preparation, the first mix of shortening and sugar is seldom creamed to its maximum air-capacity, eggs being usually added when the air content has reached 150 to 200 percent. The presence of eggs increases the ability of the shortening to absorb air and the air content at this stage will rise to 300 to 375 percent. The addition of milk and flour always entails a loss of air so that the finished batter usually contains 275 to 350 percent of air on the

basis of the shortening volume. Inferior shortenings may fail to incorporate large amounts of air, may lose air upon addition of eggs, or may lose abnormal amounts of air during the final stage when milk is added.

Considerable variations in creaming properties are encountered with different fats. Fats, to cream satisfactorily, appear to require the presence of certain highly saturated glycerides (*16*). Partial hydrogenation effectively improves the creaming qualities of oils and soft fats. Similar improvements may be obtained by the addition of a highly hydrogenated fat in small proportions. Thus, whereas lard does not cream well without prior treatment, superior creaming quality may be imparted to it by limited hydrogenation or addition of hydrogenated fat. Butter will generally be found inferior in creaming property to high grade vegetable or compound-type shortenings. It also exhibits considerable variation in this property from one lot to the next. The creaming characteristics of a few selected fats are summarized in the following table taken from Bailey (*16*).

TABLE 86.   CREAMING TESTS OF VARIOUS FATS AT 70° F.[a] (AIR INCORPORATION CALCULATED BY VOLUME, ON THE BASIS OF THE FAT)

Fat	Iodine value	Percent air incorporated, after mixing for specified times, (min.)						
		4	8	12	16	20	24	28
All-hydrogenated vegetable shortening.	62	165	215	240	265	275	280	280
Compound-type shortening "A"[b]	90	190	240	270	280	280	280	280
Compound-type shortening "B"[c]	73	150	195	230	255	270	275	275
Prime steam lard	69	85	125	145	150	155	155	155
Prime steam lard with 8% hydrogenated lard stearine added	65	155	205	235	260	270	275	275
Hydrogenated prime steam lard	61	150	200	240	260	270	275	280
All-hydrogenated vegetable shortening, untempered	62	120	160	175	180	185	185	185

[a] 1.0 lb. fat mixed with 1.5 lbs. fine granulated fruit sugar at medium speed in Hobart bench mixer with 12-qt. bowl.
[b] Compounded from slightly hydrogenated cottonseed oil and hydrogenated cottonseed oil stearine.
[c] Compounded from vegetable stearine, slightly hydrogenated cottonseed oil, and tallow.

Stabilizing Function of Fats. The stabilizing function of fats, or their tendency to impart to the cake batters sufficient strength during baking to prevent their collapse, is intimately tied up with the aerating function of fats. Considered from a physical standpoint, the cake batter is an emulsion in which fat forms the internal phase and the remaining ingredients, such as sugar, flour, milk and eggs, form the external phase. In the absence of proper aeration this emulsion will be found to become very thin and sloppy. The lack of strength is due to the diluent ingredients, especially the high sugar content, which greatly weaken the gluten struc-

ture of the dough. Fat, being plastic rather than fluid, possesses a certain amount of inherent stability. When the fat is creamed, the incorporation of air gives rise to the formation of inumerable air cells which impart considerable mechanical strength to the batter, thereby reducing its tendency to fall or collapse of its own weight during baking just prior to setting by the oven heat when the gluten structure coagulates and assumes a rigidity of its own. The finer the cellular structure of the batter, the greater will be its mechanical strength so that for this reason also optimum aeration and fat distribution should be aimed at during the creaming operation.

Once the importance of an optimum dispersion of fat in a batter is recognized, it will become clear that any factor which tends to maintain this dispersion will be of equal importance. While it is true that plastic shortening does not coalesce in a batter as would liquid oil, it does accumulate into larger agglomerates which greatly reduce the effectiveness of the emulsion. The higher the liquid and sugar content of a batter, the more difficult it becomes to maintain the emulsion in a highly dispersed state. Thus with ordinary shortening, the maximum combined milk and sugar content cannot exceed much more than 40 percent if good cake is to result. With the use of special superglycerinated shortenings possessing greatly improved emulsifying properties, the sugar and milk may be increased to as much as 50 to 55 percent of the total ingredients. The explanation for this difference in the behavior of these two types of shortenings lies in the fact that superglycerinated, or so-called high ratio, shortenings are much more finely dispersed, and remain in this condition, than are ordinary shortenings in batters of high sugar and liquid content.

Eating and Keeping Qualities. Eating quality represents a primary attribute of foods in general. The concept of eating quality covers such sensual impressions as smell, taste and cutaneous sensations. The taste, flavor, tenderness, moistness, and similar properties of cakes and other baked products are thus decisive factors which govern the acceptance or rejection of the product by the consumer. Fats contribute to eating quality principally by imparting shortness and tenderness to the baked goods. They function secondarily by making possible the use of increased proportions of such enriching ingredients as sugar, milk and eggs which enhance the taste of the products. Finally, if the fats are flavored, as is the case with butter and some lards, they also contribute importantly to the organoleptic characteristics of the product.

The keeping quality of a product is a measure of the degree of freshness retained by the product over a period of time. The duration of time during which a product may reasonably be expected to maintain freshness varies with its type. Thus, the rate at which bread, for example, loses

freshness differs considerably from that at which crackers become stale. The palatability of bread is seldom expected to extend over more than three to four days after baking, while crackers are frequently consumed weeks and even months after baking. The rate of staling in a given product may be influenced by ingredients and method of production. In the case of cakes, for example, the inclusion of relatively large proportions of fat tends to reduce the rate of staling, or at least the appearance of characteristics normally associated with true staling, such as loss of moisture, tenderness and flavor. It is not uncommon to have cakes rich in shortening retain their palatability for a week or more, although there is an inevitable reduction in quality which is the more marked the longer the cake is held. Cakes in which an insufficient amount of shortening is used will stale more rapidly and will therefore have a reduced shelf-life.

Function of Fat in Bread Dough. A few years ago the suggestion was advanced that if shortening were finely dispersed in part of the dough water by means of a homogenizer it would result in a more uniform and thorough distribution of the fat in the dough and hence increase the effectiveness of the shortening. Careful subsequent investigations of this procedure failed to substantiate the claims of its proponents. This is not surprising in view of the fact that during high speed mixing of bread doughs the shortening is spread largely in the form of monomolecular films along the interfaces of gluten and starch and hence attains a degree of dispersion far in excess of any that may be achieved by mechanical homogenization (*265*). Evidence has been developed (*266, 267*) which indicates that fat and gluten form a combination in mixed dough which it is difficult to break down. Thus, whereas ethyl ether will extract about 70 percent of the fatty materials from flour itself, only 30 percent of fat can be extracted after the flour has been mixed into a dough. It has also been found that the same holds true of added nonflour fats. If a dough is made with additions of mineral oil, oleic acid, or related materials, and then dried, most of the added oil cannot be recovered with ethyl ether. Furthermore, when starch-gluten separations are made with such doughs, the "bound" oil is found to stay with the gluten. It is as yet not known whether fatty materials play an essential role in the bread-making properties of flours.

The functions of shortening in bread doughs have been reviewed by Carlin (*265*). The addition of fats to doughs in amounts ranging from 2 to 6 percent produces the following effects upon the various physical characteristics of bread: Loaf volume is increased perceptibly, the increase being progressive up to 2 percent addition with normal flours and up to 3 to 4 percent with certain high protein flours. Bread texture is made appreciably softer and more velvety, the effect being progressive

with increasing shortening additions up to 5 to 6 percent of flour weight. Increments of fat between a range of 2 to 5 percent produce a more uniform cell structure. Higher percentages may render the grain more coarse with fairly thick cell walls. Increasing fat contents also have a tenderizing effect upon the crumb and crust of the bread, imparting at the same time a more brilliant sheen to the crumb and a lustrous, richer appearance to the crust. Fat also improves the keeping quality of bread, the
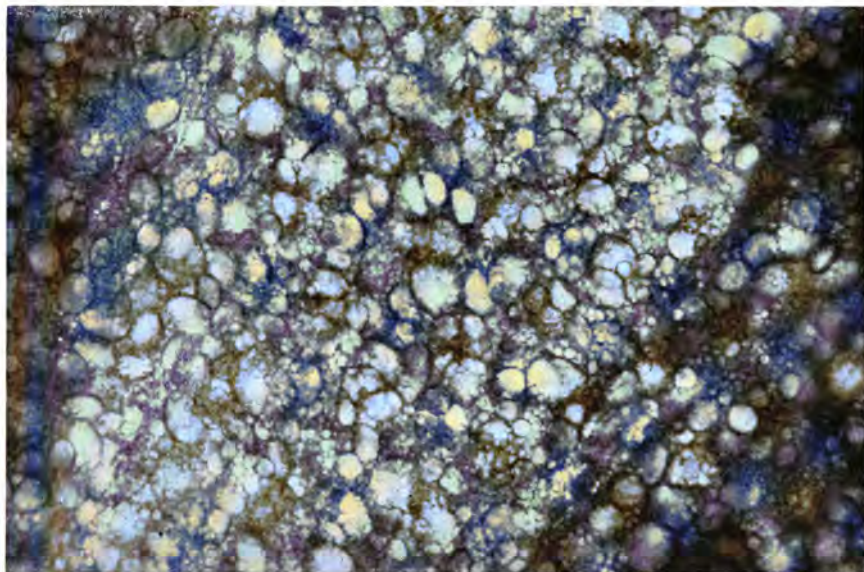

FIG. 45—Microphotograph of bread dough (200 × mag.) showing the dark gluten strands enmeshing starch granules. The fat is located on surface of gluten strands. (*Courtesy Swift & Co.*)

effect being progressive so that loaves containing 6 percent shortening will have superior keeping quality to loaves containing 3 to 4 percent, and the latter again being superior to loaves containing only 1 percent when the loaves are tested for softness after 72 to 96 hours storage time.

EMULSIFYING AGENTS

Emulsifying agents are used extensively by the baking industry as dough and bread improvers. Emulsifiers include a wide variety of products all of which are characterized by possessing surface active properties. This surface action derives from the fact that emulsifiers are composed of two distinctly different radicals, one of which consists generally of one or two long fatty acid chains such as occur in natural fats, while the other may be one of a variety of organic or inorganic combinations of either

natural or synthetic origin. The fatty acid radical constitutes the non-polar or hydrophobic group of the molecule and exhibits ready solubility in fats and oils, while the other radical shows polar or hydrophilic characteristics and hence affinity for polar substances, such as water. Thus when an emulsifying agent is introduced into a system consisting of a mixture of polar and non-polar materials, such as an oil and water mixture, it will concentrate at the surface or interface, with the non-polar portion of its molecules dissolved in the oil phase and the polar portion protruding into the aqueous phase, reducing thereby the surface tension and stabilizing the emulsion. The mechanism of this action is treated in greater detail in the section on EMULSIONS. In recent years principal interest has centered on three kinds of products, namely the lecithins, the mono- and diglycerides, and the polyoxyethylene types of compound.

Lecithins are phosphatides closely related to fats and are therefore also called phospholipids. They differ from normal fats by having one of the fatty acid chains of the triglyceride substituted by a phosphocholine radical as shown by the following formula of a typical lecithin:

$$
\begin{array}{c}
\text{H} \qquad\; \text{O} \\
| \qquad\;\; \| \\
\text{HC—O—C—C}_{17}\text{H}_{33} \\
| \qquad\;\; \text{O} \\
\qquad\;\; \| \\
\text{HC—O—C—C}_{17}\text{H}_{33} \\
| \qquad\;\; \text{O} \\
\qquad\;\; \| \\
\text{HC—O—P—O—CH}_2\text{CH}_2\text{—N(CH}_3\text{)}_3 \\
\text{H} \quad | \qquad\qquad\qquad | \\
\qquad \text{OH} \qquad\qquad\quad \text{OH}
\end{array}
$$
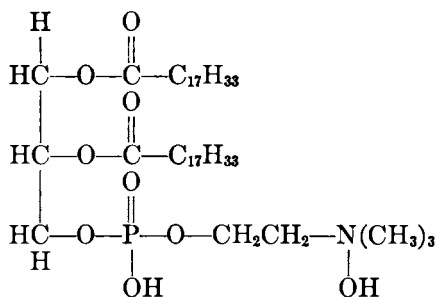
When a lecithin is completely hydrolyzed it yields glycerol, fatty acids, phosphoric acid and choline. Choline is a colorless, viscid, strongly alkaline liquid with the following chemical formula:

$$
\begin{array}{c}
\text{(CH}_3\text{)}_3 \\
| \\
\text{N—OH} \\
| \\
\text{CH}_2 \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$
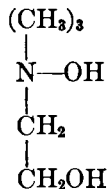
It is classified as a vitagen, i.e., a substance essential to the normal physiological functioning of the animal organism and has been tentatively included as a member of the vitamin B complex. Choline deficiency in such animals as dogs, rats and chicks causes pronounced pathological systems. Its requirements for man are still not known. Because differ-

ent fatty acids may constitute the fatty portion of the lecithin molecule, a large number of different lecithins are found in nature where they form an indispensable component of practically all vegetable and animal cells, especially in the brain, heart, kidney, liver, egg yolk and bone marrow. Lecithins are normally associated with cephalins, which are closely related compounds, differing from the lecithins only by having the phosphoric acid esterified with colamine ($CH_3CH_2NH_2$) instead of choline. The emulsifying function of lecithin becomes readily apparent from a consideration of its formula. The two fatty acid radicals form the hydrophobic group of the compound and exhibit a strong affinity for fats, while the phosphocholine radical constitutes the hydrophilic group and has a strong affinity for water. Thus in any mixture of water and oil, the lecithin will exhibit a pronounced emulsifying action by reducing the surface tension at the interfacial boundaries existing between the oil and the water phases. This results in two distinct effects; it facilitates the dispersion of one phase in the other, and it prevents the dispersed droplets from recombining or coalescing, i.e., the emulsion is stabilized.

Commercial lecithin is obtained chiefly from corn and soybean oil and consists of a mixture of lecithins, cephalins, glycosides and other phosphatides. Schofield and co-workers (*268*) have estimated the approximate composition of a commercial soybean lecithin to be 29 percent lecithin, 31 percent cephalin and 40 percent inositol-containing phosphatides. Thornton, Johnson and Ewan (*269*) have determined the fatty acid composition of a highly purified lecithin, consisting of 97 percent lecithin and 3 percent cephalin, with the following results:

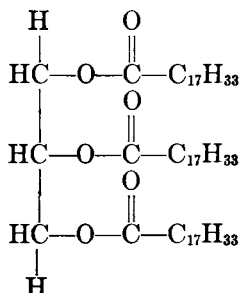TABLE 87. FATTY ACID COMPOSITION OF
LECITHIN

	Percent
Palmitic acid..................	15.77
Stearic acid...................	6.30
Oleic acid....................	12.98
Linoleic acid.................	62.92
Linolenic acid................	2.02

Commercial lecithin usually contains 35 to 40 percent of corn or soybean oil which serves as a solvent and carrier for the phosphatides and further acts as a protective medium against oxidation. In appearance it is a gummy brown material of soft consistency and possesses a slightly sticky character. It is readily soluble in fats and oils, but insoluble in water; hence in practice the material is first incorporated with baking fats before being added to doughs or batters. The product is commercially available in various modified preparations marketed under different trade names.
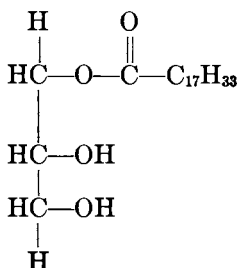
The amounts of lecithin used in individual batches are very small. In products in which the fat content is less than 8 percent, the recommended lecithin level ranges from 2 to 3 ozs. per 100 lbs. of flour, while in high fat products, it is from 1 to 2 percent based on the shortening employed. The use of lecithin in bread doughs is said to increase fermentation tolerance, produce better dough machineability, yield a more uniform crust color, give a more tender crust and a smoother texture with a more uniform grain, and produce a softer and less rapidly staling loaf. Walrod (*270*) has described extensive bread baking tests using lecithin in amounts of 1 to 5 oz. per 100 lbs. of flour, arriving at the following conclusions: lecithin permits some reduction in mixing time and a slight increase in absorption, yielding doughs which feel drier, possess improved machineability and show greater elasticity and smoothness with the almost complete absence of buckiness regardless of the type of flour used. Lecithin-containing doughs produce more uniformly shaped loaves possessing a more even grain and a finer texture. Lecithin was also found to contribute to a retention of freshness in bread. Pratt (*271*) has studied the effect of additions of lecithin upon the physical characteristics of dough and baked bread. According to his findings, the presence of 0.25 percent of lecithin in dough, which proved to be the optimum level, effected a slight mellowing of the gluten and an increase in the mixing tolerance of the flour. The most noticeable result of lecithin addition to the dough was an improvement of its handling properties at the make-up. The doughs were rendered more elastic and lively, with a distinctly drier feel. Dusting flour requirements were reduced and the skin formed in the molding operation showed less signs of tenderness. The presence of lecithin did not produce measurable effects upon absorption, fermentation, proof and baking times. In the finished product, volume and crumb color remained unaffected. The notable improvements were a more tender crust, finer grain and texture, more symmetrical appearance, and a longer keeping quality. A loaf containing 0.3 percent lecithin with 1 percent shortening had keeping qualities equivalent to those of a lecithin-free loaf containing 4 percent shortening. But a loaf with 3 percent shortening and 0.25 percent lecithin exhibited superior keeping qualities. Bradley (*272*) measured the effect of surface active agents upon crumb compressibility and failed to observe any significant crumb softening effect with lecithin. With respect to cake products, the use of 1 to 2 percent of lecithin based on the shortening is said to result in freer flowing batters, more uniform color, smoother texture and more uniform grain, better keeping quality and greater flavor stability.

Monoglycerides and diglycerides are fats differing from a typical fat molecule in which there are three fatty acids combined with a glycerol
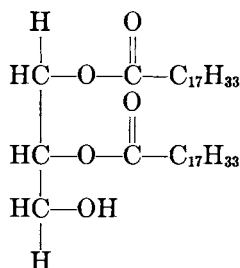
radical, whereas in a monoglyceride there is only one fatty acid, and in a diglyceride there are only two fatty acids combined with the glycerol radical. Thus a representative formula of a triglyceride fat molecule would have the following form:

$$
\begin{array}{c}
\text{H} \quad\quad \text{O} \\
\mid \quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \quad\quad\quad \text{O} \\
\quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \quad\quad\quad \text{O} \\
\quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \\
\text{H}
\end{array}
$$

while the corresponding mono- and diglycerides would have formulas as follows:

$$
\begin{array}{cc}
\begin{array}{c}
\text{H} \quad\quad \text{O} \\
\mid \quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \\
\text{H}\overset{}{\text{C}}\text{—OH} \\
\mid \\
\text{H}\overset{}{\text{C}}\text{—OH} \\
\mid \\
\text{H}
\end{array}
&
\begin{array}{c}
\text{H} \quad\quad \text{O} \\
\mid \quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \quad\quad\quad \text{O} \\
\quad\quad\quad \parallel \\
\text{H}\overset{}{\text{C}}\text{—O—}\overset{}{\text{C}}\text{—C}_{17}\text{H}_{33} \\
\mid \\
\text{H}\overset{}{\text{C}}\text{—OH} \\
\mid \\
\text{H}
\end{array} \\
\text{Monoglyceride} & \text{Diglyceride}
\end{array}
$$

Mono- and diglycerides have generally been assumed to be absent in natural fats which have not been subject to hydrolysis. However, Carlin (*273*) has given the following percentages of mono- and diglycerides as being naturally present in various fat products:

TABLE 88.   MONO- AND DIGLYCERIDE CONTENT OF
VARIOUS FAT PRODUCTS

	Percent
Steam rendered lard	0.15- 0.80
Hydrogenated vegetable shortening...	0.36- 0.49
Margerine	0.70- 1.10
Butter	0.30- 0.61
Refined cottonseed salad oil	0.45- 0.53
Refined soybean oil	0.90
Crude peanut oil	0.5- 8.0

The presence of mono- and diglycerides in hydrogenated shortening greatly increases the emulsifying power of the shortening with liquids, thereby permitting ratios of sugar to flour as high as 140 percent without reducing the volume or lightness of the baked product. The increased emulsifying power of these so-called superglycerinated fats is accounted for by the fact that the mono- and diglycerides are interface modifiers between aqueous and oleaginous media by possessing both hydrophilic and lipophilic properties. The hydrophilic character is contributed by the OH or hydroxyl group or groups of the glycerol radical, while the lipophilic character results from the fatty acid portion. Gaffney (*274*) has described the various methods whereby mono- and diglycerides may be produced in hydrogenated shortening. These include (1) heating triglycerides with glycerin to form a mixture and mono- and diglycerides; (2) hydrogenating an unsaturated fatty oil to an iodine value of 40 or lower and then reacting it with glycerin until it contains at least 19 percent of combined glycerin (triglycerides contain about 10.3 percent, diglycerides 14.8 percent and monoglycerides about 25.7 percent), the synthetic hard fat being then mixed with a fatty oil such as cottonseed, or with stearine which is then blended with the oil. The mixture may then be further hydrogenated to obtain the desired consistency. (3) Mono- and diglycerides may also be prepared by polymerizing pure glycerin to polyglycerols and heating these with oleic and stearic acids to form a mixture of glycerol mono- and dioleate and glycerol mono- and distearate which may then be added to hydrogenated shortenings. Although the esters of glycerol are most commonly used for incorporation in shortenings, the esters of mannitol and sorbitol or of the glycols may also be used. Mono- and diglycerides are sold to bakers under a number of proprietary names as mixtures containing varying proportions of the two substances, usually with the addition of diluents in the form of fats or some farinaceous material. A recently introduced emulsifier used for bread doughs and cake batters consists of the diacetyl tartaric acid ester of mono- and diglycerides.

High-absorption shortenings are used primarily for the production of fine cakes, although they also find some application in the production of yeast-raised sweet goods and prepared flour mixes. Because of their low smoke point they are unsuitable for deep fat frying.

According to Gaffney (*274*) even the mineral acids may play a role in the manufacture of high absorption shortenings. If sulfuric acid is added to oleostearine, cocoa butter or hydrogenated cottonseed oil, a sulfated triglyceride is formed with a molecular formula having at least one sulfate group attached to a carbon at a double bond of an unsaturated fatty acid radical. These sulfated triglycerides, either alone or mixed with fatty

acid, are effective in promoting emulsification of the cake batter ingredients and permit a high ratio of liquid to flour.

Recently compounds have been introduced which are primarily designed to function as bread softeners and anti-staling agents. While a variety of these synthetic emulsifiers have been produced, their general nature can be readily illustrated by taking as an example the most widely used product, namely polyoxyethylene monostearate.

This emulsifier consists of ethylene glycol polymers of ethylene oxide esterified with stearic acid. Ethylene glycol is a polyhydroxy alcohol having the formula:

$$\begin{array}{c} H_2C\text{——}CH_2 \\ | \quad\quad | \\ OH \quad OH \end{array}$$
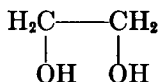
It is colorless syrupy liquid, completely soluble in water and alcohol, and possesses a sweet taste. It is commonly used as an anti-freeze compound and is reported to be about as toxic as methyl or wood alcohol. In the production of the emulsifier it is made to react with ethylene oxide $(H_2C\text{—}CH_2)$, a gas whose common use is that of a fumigant with food-

$$\begin{array}{c} \diagdown\diagup \\ O \end{array}$$

stuffs and grains, to form polymers of varying lengths. The polymers in turn are reacted with stearic acid to form the polyoxyethylene monostearate ester having the following representative formula:
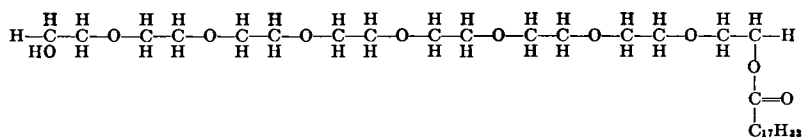
It is also possible to first react stearic acid with ethylene glycol to form ethylene glycol monostearate and then reacting this compound with ethylene oxide to form a mixed polymer of the desired average length. Other types of synthetic emulsifiers include fatty acid esters of mannitol and sorbitol which are combined with polymers of ethylene glycol. Mannitol and sorbitol are, like glycol, polyhydroxy alcohols obtained by the electrolytic reduction of glucose. Thus in the manufacture of these latter types of products the starting material is dextrose which is reduced to sorbitol and then esterified with fatty acids. The ester is then treated with ethylene oxide to produce the emulsifier. None of the commercial compounds are chemical entities but represent mixtures which can be closely reproduced. They are offered to the baking industry under a variety of trade names, although their general function in dough and cake batters is

essentially the same.   Because of the fact that their synthesis involves the use of toxic materials, the question of toxicity of the end-products themselves has received considerable study.   Numerous feeding trials, both with laboratory animals and human beings, and involving the use of these chemicals at levels normally encountered in baked products, have failed to disclose toxic properties, although the evidence accumulated at the time of this writing (1951) has not been considered conclusive by a number of responsible quarters.

CHAPTER XII

MILK AND MILK PRODUCTS

The use of milk of different mammals as food for man appears to date back to early history. Jacobs (*275*) states that milk of domestic animals was in common use as a food some 6,000 years ago. While the cow at present is the most efficient and certainly the most important milk-producing animal, it may be mentioned in passing that other animals, such as the goat, sheep, buffalo, llama, reindeer, horse, ass and camel all serve as suppliers of milk for human consumption in different parts of the world. Since our interest here centers exclusively upon cow's milk, both in its natural fresh state and its various prepared forms, the following discussion refers only to this type of milk.

COMPOSITION OF MILK

If fresh milk is superficially examined, it will appear only as a white fluid possessing a faint pleasant odor and a slightly sweet and characteristic taste. The first indication that milk is not a simple product is obtained when it is permitted to stand for a period of several hours. The appearance of the so-called "cream line" is then observed, indicating that milk contains a certain amount of fat which is lighter in density than the remaining portion and hence rises to the surface. If the milk is kept at room temperature for several days, another prominent change will be observed. Both its taste and odor will have assumed a distinctly sour character and the solid constituents will have separated from the liquid in the form of a white curd suspended in a relatively clear fluid. Thus even casual observation of milk at different stages of holding clearly indicates that it is not a simple product.

To really appreciate the complexity of the composition of whole milk we must turn to the findings of scientific research. These have been recorded in several excellent monographs, notably those by Davies (*276*), Eckles, Combs and Macy (*277*), Associates of Rogers (*278*), and Lampert (*279*).

The following table, cited from Jacobs (*275*), lists the various constituents present in milk and grouped according to the principal fractions in which they occur.

TABLE 89. COMPOSITION OF MILK

Fraction	Component
Lipid	Consists of fat composed of the mixed triglycerides of the following fatty acids in order of importance: oleic, palmitic, myristic, stearic, and butyric; of lesser importance—caproic, caprylic, lauric, capric, and arachidonic. In addition, the oil-soluble vitamins, cholesterol, xanthophyll, cephalin, and lecithin are present.
Protein	Casein, lactalbumin, and lactoglobulin. These proteins contain some 20 or more amino acids including all of the essential ones.
Carbohydrate	Lactose or milk sugar.
Mineral	Sodium, potassium, calcium, and phosphorus, chlorine, and sulfur in substantial quantities. Magnesium, copper, iron, zinc, manganese, and iodine in smaller amounts. Carbonates are also present.
Vitamin	Vitamin A and its precursors such as carotene, thiamine, ascorbic acid, vitamins D, vitamins E, riboflavin, niacin, pantothenic acid, and pyridoxine are present.
Enzyme	Phosphatase, amylase, lipase, catalase, peroxidase, galactase, reductase.
Other Organic	Citric and lactic acid, creatine, creatinine, urea, choline.
Gas	Carbon dioxide, oxygen, and nitrogen.
Water	

From a quantitative standpoint, water represents the largest single component of milk, constituting on an average some 87.5 percent. The remaining 12.5 percent of total solids are made up of protein, approximating 3.4 percent, the milk sugar lactose, which averages about 4.75 percent, milk fat in an amount of 3.65 percent, and ash amounting to some 0.70 percent. The composition of milk is subject to some variations induced by different environment, breed of animal and its management. Differences due to breed appear to be the most pronounced. Thus Gamble and co-workers (*280*), comparing the average monthly composition of Holstein and Jersey cows' milks, have found that Jersey cows consistently produced milk with a higher fat content than did Holstein cows, the actual average values being 5.3 and 3.4 percent, respectively. The same held true of the protein, lactose and ash contents, though to a less marked degree. On the whole, milk of Jersey cows contained 2.42 percent more total solids than did milk of Holstein cows, a difference which is quite significant. Other factors which have been found to affect the composition of milk include, among others, the individuality of cows, frequency of milking, period of lactation, season of the year, kind and quality of feed. They are discussed in detail by Davies (*276*).

INDIVIDUAL CONSTITUENTS OF MILK

Milk Fat or Butterfat. The general nature of fats and oils forms the subject matter of a separate chapter in which the composition of

butterfat is also given. These aspects will hence not be discussed here. Milk fat occurs in fresh milk which has not been agitated in the form of minute fat globules varying in size from 0.1 to 10 microns, with an average of 3 microns. The extremely small size of these globules becomes more clearly apparent when the fact is considered that 1 cc. of milk contains anywhere from 2 to 4 billion globules. When milk is agitated there is a tendency for the fat globules to clump together to form aggregates of larger size in which the individual globules still retain their separate structures. The tendency of milk to cream, or for the fat to separate in the form of cream, is made possible by the lower specific gravity of the fat (which is of the order of 0.92 to 0.94, according to temperature) as compared with milk serum (which is over 1.03). It has been found that during creaming the fat globules do not rise individually but in the form of clumps. Raw milk creams more readily than heated milk because it contains a large number of these clumps, whereas heated milk has only a few as heating destroys the clumping of fat globules.

When cream is agitated or churned at a proper temperature, the fat globules clump together, forming progressively larger and larger aggregates or fat clusters. A point is finally reached where the ratio of the surface area of the fat clumps to their volume is relatively small and the emulsion breaks, the fat grains separating from the surrounding liquid in the form of a plastic material, the familiar butter. Churning, by an action not yet fully understood, thus inverts the oil-in-water system represented by cream into a water-in-oil system represented by butter. Butter may be considered a solid system of a continuous fat-phase in which are dispersed fat, water, and air-globules, each type being stabilized by an envelope of hydrated proteins.

Butterfat has associated with it in milk a number of different fat-soluble substances which are generally present in relatively minute amounts. They include the yellow coloring substances carotene and xanthophyll, the monohydroxy alcohol cholesterol, the phospholipids lecithin and cephalin, and the fat-soluble vitamins A, D and E. The carotene and xanthophyll content of milk is derived from vegetable matter consumed by the animal, the animal organism being unable to synthesize these substances. It is these yellow coloring substances which impart the natural tint to butter. This accounts for the fact that summer butter, obtained at a period when cows feed on pastures, has a much richer yellow color than winter butter. Carotene is an important precursor of vitamin A, whereas xanthophyll does not possess vitaminic properties.

Cholesterol $(C_{27}H_{45}OH)$ is representative of a group of substances known as the sterols which are usually classed together with true fats, principally because both groups are soluble in fat solvents. There is,

however, no structural similarity between them. The sterols are mono-hydroxy alcohols possessing rather complex ring structures. They are widely distributed in nature, the so-called phytosterols occurring in plants, and cholesterol in animals where they are found in brain tissue, nerves, blood and liver. Structurally, cholesterol closely resembles certain important hormones. The cholesterol content of butter fat has variously been reported to range from a low of 0.071 to a high of 0.43 percent (*276*).

The phospholipids are mixed glycerides in which one of the hydroxyl groups of glycerol is substituted by a radical consisting either of choline and phosphoric acid or of amino-ethyl alcohol and phosphoric acid, with the two remaining hydroxyl groups of the glycerol being substituted by fatty acids. The choline containing glycerides are the lecithins, whereas the amino-ethyl alcohol phosphatids are the cephalins. Phospholipids occur in milk in very small amounts, seldom exceeding 0.1 percent. The fishy odor and taste which occasionally develop in butter and dry milks of high moisture content have been attributed to the hydrolysis and oxidation of lecithin which result in the chemical breakdown of the choline portion into trimethylamine which, at ordinary temperatures, is a gas possessing a pronounced "fishy" odor.

The three fat-soluble vitamins of milk, namely vitamins A, D and E, are discussed in some detail in a separate chapter. Being fat-soluble, they are naturally associated with the fat-portion of the milk and are removed almost entirely with the cream portion when the milk is separated. Non-fat milks, therefore, do not contain significant amounts of these fat-soluble vitamins.

Lactose or Milk Sugar. The principal carbohydrate of milk is lactose or milk sugar which is present in cow's milk in the average amount of 4.8 percent. Chemically considered, it is a disaccharide yielding upon hydrolysis a molecule of glucose and a molecule of galactose. Its structural formula has been determined to be as follows:

Galactose part　　　　Glucose part
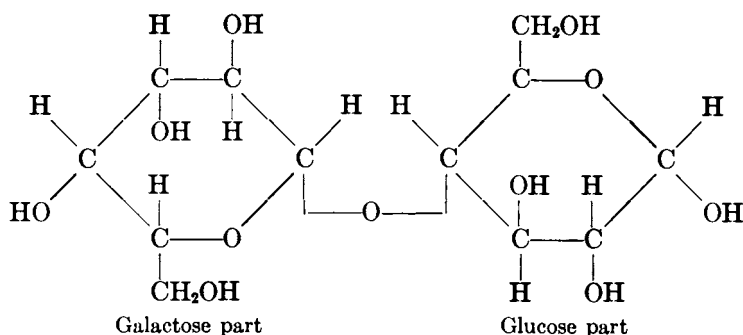
Lactose, $C_{12}H_{22}O_{11}$

Lactose is a reducing sugar of relatively low sweetness, having a value of about 16 as compared to 100 for sucrose. It is not very soluble and may crystallize out in sweetened condensed milk, giving that product a "sandy" taste. It is fermentable by certain types of yeast and bacteria into carbon dioxide and alcohol. Lactic acid bacteria convert it into lactic acid in a fermentation process which also yields butyric acid and carbon dioxide as by-products. The curdling of milk upon souring, or lactic acid fermentation, is due to the coagulation of the protein casein when a pH value of 4.6 is reached or at an acidity of 0.5 to 0.7 percent. Sourness in milk is detectable by taste when its lactic acid content reaches the level of 0.25 to 0.30 percent.

Normal milk also contains very small amounts of glucose. Sweetened condensed milk is prepared by the addition of sucrose and evaporation, so that the finished product contains, in addition to lactose, considerable amounts of sucrose and small amounts of fructose and glucose which result from the hydrolysis of the sucrose.

Proteins. The principal protein of milk is casein, which is present in the average amount of 2.7 percent. Milk also contains approximately 0.5 percent lactalbumin and 0.5 percent lactoglobulin. The amino acid composition of casein and lactalbumin is given by Davies (*276*) as shown in Table 90.

From this table it will be seen that casein contains all of the essential amino acids namely, histidine, lysine, tryptophane, phenylalanine, methionine, threonine, leucine, isoleucine and valine. It will also be noted that casein is a phospho-protein, that is, it contains a phosphoric acid radical in its chemical structure. In fresh milk the protein is combined with calcium as calcium caseinate. When casein is acted upon by the enzyme rennin, it is precipitated out of solution by calcium in the form of calcium paracaseinate. It is also precipitated out of solution in its free condition when the pH value of milk, which is normally 6.6, is reduced to 4.6, the isoelectric point of casein, either by the addition of acid or by allowing the milk to sour by lactic acid fermentation. The molecular weight of casein has been estimated to be 75,000-100,000.

In addition to casein, milk further contains small quantities of lactalbumin and lactoglobulin. The amino acid composition of lactalbumin is given in Table 90. This protein, which is present in milk in the average amount of 0.5 percent, is heat-coagulable and undergoes some degree of coagulation when milk is heated, as in dry milk production. Protein coagulation is accompanied by a loss in solubility in water. Lactoglobulin, which is present in milk in extremely small amounts, is also a heat-coagulable protein.

The difficulty with which milk fat is extracted from milk by fat sol-

vents and the fact that the fat globules fail to coalesce to form large masses of fat when the milk is not agitated have long been explained by the assumption that the fat globules are surrounded by a protein film. The existence of such a membrane is now confirmed and Palmer (*281*) has reported it to be about 10 millimicrons (about 1/2,500,000 inch) thick. This film, to which the term lactomucin has been given, is rich

TABLE 90. AMINO ACID COMPOSITION OF CASEIN
AND LACTALBUMIN
(Percentages of Proteins)

Amino Acids	Casein	Lactalbumin
Glycine.....................	0-0.4	0.4
Alanine....................	1.5-1.8	2.4
Valine.....................	7.2-7.9	1.0-3.3
Leucine....................	9.3-10.5	14 -19
Phenylalanine...............	3.2-3.9	1.2-2.4
Tyrosine...................	4.5-6.5	0.9-1.9
Serine.....................	0.4-0.5	1.8
Threonine..................	3.9	5.3
Isoleucine..................	6.5	0
Cystine....................	0.25	1.7-4.0
Proline....................	7.6-8.7	3.8-4.0
Hydroxyproline.............	0.2	?
Glutamic acid...............	20.0-21.8	10.1-12.9
Hydroxyglutamic acid.......	10.5	10.0
Aspartic acid...............	1.4-4.1	1.0-9.3
Tryptophane...............	1.5-2.2	2.7
Arginine...................	3.8-5.2	3.0-3.5
Histidine...................	2.5-3.4	1.5-2.6
Lysine.....................	6.0-7.6	8.4-9.9
Methionine.................	0.4	?
Dodecanoamino acid.........	0.75	?
Ammonia...................	1.6	1.3
Phosphorus................	0.85	—

in phosphorus compounds of the lecithin type. In butter making, a large portion of this protein material is removed from the fat and left in the buttermilk.

The Minerals of Milk. Milk contains significant amounts of essential minerals, the most important these being calcium, phosphorus, magnesium, potassium, sodium, chlorine and sulfur. The ash content of milk is generally found within the range of 0.6 to 0.9 percent, with an average at 0.72 percent. The percent composition of the ash is given in Table 91 in which are compiled the ranges of values obtained by various investigators (*275*).

It will be noted that approximately one half the ash is composed of

calcium phosphate. Davies (*276*) points out that of all the radicals present, phosphoric acid is present in greatest equivalent, while of the metallic radicals calcium is present in greatest equivalent, followed closely by potassium. Sodium is present in roughly half the equivalent of potassium. Chloride is a rather variable constituent and is present from a third to a half of the equivalent of phosphoric acid. Not all of the minerals are in true solution. Part of the calcium, magnesium and phosphate are organically bound to the proteins of milk. In addition to the above mentioned minerals, milk also contains trace amounts of copper, iron, zinc, manganese, aluminum, and iodine. Although these latter mineral elements are present in an amount totaling only about 20 p.p.m. (0.002 percent), they are nevertheless of nutritional significance. Citric acid

TABLE 91. THE COMPOSITION OF THE ASH OF
MILK

Mineral	Ranges of values found by several European investigators, %
Potassium	14.6 -23.9
Calcium	14.2 -20.5
Sodium	1.93 - 8.2
Magnesium	0.72 - 3.1
Iron	0.035- 0.280
Phosphorus	9.44 -12.8
Chlorine	12.2 -16.4
Sulfur	1.53 - 2.46

($C_6H_8O_7$) does not show up in normal ash determinations because it is destroyed in the ashing of milk. It is, however, an important component in milk in relation to salt equilibria. The average citric acid content of milk has been reported to be approximately 0.02 percent.

Enzymes. Milk contains a considerable number of enzymes, the principal ones being lipase, amylase, phosphatase, peroxidase and catalase. Other enzymes whose presence in milk has been reported are oleinase, butyrinase, galactase, lactase and reductase. Since enzymes are sensitive to heat, they are largely inactivated during milk pasteurization or the heating incidental to the production of dry milks. Lipase, the fat-splitting enzyme, may occasionally give rise to off-flavors in milk.

Vitamins of Milk. Milk contains a variable vitamin content which depends to a marked extent upon the type and quality of feed given to the cow. Well-fed animals generally give milk which is rich in vitamin A. Milk is also an excellent source of riboflavin, and a fair source of thiamine. Although the presence in milk of such other B vitamins as

niacin, pantothenic acid, and pyridoxine has been established, their respective amounts are of a low order. Milk is a fair source of vitamin C and a poor source of vitamin D. Market milk is generally fortified with the latter factor by one of several methods developed for that purpose. The vitamin E content of milk is also low.

Sharp, Shields and Stewart (*282*) examined a large number of samples of dry whole milk for their vitamin contents. The values which they found are summarized in the following table.

TABLE 92.   VITAMIN CONTENT OF DRY MILK

Vitamin	No. samples examined	Range or average per 100 g. of whole milk
Vitamin A..............	200	495–1,620 I.U.
Thiamine...............	700	0.22–0.35 mg. (0.29 mg. avg.)
Riboflavin.............	500	1.115–2.01 mg. (1.55 mg. avg.)
Vitamin C.............	1,000	0–13.6 mg. (9.6 mg. avg.)
Niacin.................	180	0.5–0.9 mg. (0.69 mg. avg.)
Ca Pantothenate.........	156	2.9 mg.
Biotin.................	76	41 μg.
Pyridoxine.............		0.24–0.46 mg. (0.33 mg. avg.)
Choline................		89 mg.

Except for vitamin C, none of the vitamin values showed a decrease when the milk powder samples were stored for six months or more under air or an inert gas.

Buttermilk. Buttermilk is the liquid remaining after the removal of the fat from the milk or cream in the process of churning butter. If the butter is made from sweet cream, the resultant buttermilk is very similar to skim milk in its composition and characteristics. If sour cream was used for butter making, the buttermilk will contain lactic acid which imparts to it its characteristic sour taste, and somewhat less lactose than is present in sweet buttermilk. Except for its reduced fat and vitamin A contents, genuine buttermilk has about the same composition and nutritive value as whole milk. It is somewhat richer in phospholipids, since these substances are retained by the buttermilk on churning. The average composition of buttermilk is given in the following table:

TABLE 93.   AVERAGE COMPOSITION OF BUTTERMILK

	Water %	Protein %	Fat %	Lactose %	Ash %	Lactic Acid %
Sweet buttermilk....	90.83	3.45	0.55	4.40	0.73	0.04
Sour buttermilk.....	91.30	3.40	0.65	3.40	0.65	0.60
Buttermilk solids....	2.0	37.6	5.9	42.50	7.55	5.50

Buttermilk is used fairly extensively by bakers in the production of a variety of products. Dried sweet buttermilk, produced either by the roller or spray process, may be safely regarded as interchangeable with nonfat dry milk solids. It contains between 1 to 2 percent of phospholipids and considerably more fat (4.6 to 6.0 percent) than does nonfat dry milk. Dried sour buttermilk, because of its increased acidity and pronounced flavor, is used to a greater extent in dark breads, such as rye and whole wheat breads, in dark cakes and cookies, and in prepared biscuit and pancake mixes. Because of the variability in the acidity of buttermilks coming from different processing plants, modern methods of producing dried acid buttermilk designed for bakery use call for the controlled souring of sweet cream buttermilk to a predetermined acidity and blending with sweet whey solids and flour (*283*).

Whey. Whey is the product which remains after the removal of most of the casein and fat from milk in the process of cheese making. Whey is relatively rich in lactalbumin, lactose and mineral matter. The average composition of whey products is given in the following table (*279*).

TABLE 94. AVERAGE COMPOSITION OF WHEY PRODUCTS

	Water %	Protein %	Fat %	Lactose %	Ash %	Lactic Acid %
Cheese Whey............	93.0	0.9	0.2	4.8	0.5	0.6
Condensed Whey.........	55.5	8.0	1.5	28.0	5.5	1.5
Dried Whey.............	3.0	12.2	2.7	68.8	10.4	2.9

Large quantities of whey are dried or condensed for use as animal feed. Its utilization in the baking industry is limited principally to that of an added ingredient to various milk products, such as dried buttermilk, nonfat dry milk solids, and other products sold in the form of proprietary mixtures. It is seldom used as a direct baking material.

CLASSIFICATION OF MILKS

The Federal Food, Drug and Cosmetic Act defines milk as follows:

"Milk is the whole, clean lacteal secretion obtained by the complete milking of one or more healthy cows, properly fed and kept, excluding that obtained within 15 days before and 5 days after calving or such longer period as may be necessary to render the milk practically colostrum-free." Colostrum is a thick viscous fluid differing greatly in composition from that of normal milk. It is secreted for a short period after the birth of a calf and is characterized by a higher proportion of albumin and globulin, a higher percentage of ash and chloride and a lower lactose

content. While highly beneficial for calves, colostrum is thought to be unsuitable for human consumption.

Pasteurized milk is milk which has been heated to 140° F. for 30 minutes and then quickly cooled to 50° F. or lower. Pasteurization may also be carried out by heating milk to a higher temperature, such as 161° F., for very brief periods of 15 to 20 seconds. These conditions of temperature and time assure the destruction of pathogenic bacteria which may be encountered in milk. Pasteurization is now universally practiced.

In recent years a fair proportion of marketed milk has been reaching consumers in homogenized form. Homogenization, carried out in a special unit called a homogenizer, in which the milk is forced through a minute orifice by the application of high pressure, effects a reduction in the size of the fat particles so that they no longer form a cream layer. The U.S. Public Health Service defines homogenized milk as milk which has been treated in such manner as to cause a breakup of the fat globules to such an extent that after 48 hours' storage there is no visible cream separation, and the fat content of the top 100 cc. of milk in a quart bottle does not differ by more than 5 percent from that of the remaining well-stirred milk.

Milk is graded according to standards established by the U.S. Public Health Service, the principal basis being the bacterial content of the milk, provided the milk is produced upon dairy farms conforming with all of the items of sanitation given in the regulation. The grades are: Grade A raw milk, Grade B raw milk, Grade C raw milk, Grade A pasteurized milk, Grade B pasteurized milk, and Grade C pasteurized milk. It is recommended that Grade B milk be always pasteurized and that Grade C milk, both raw and pasteurized, be not used for human consumption.

Certified milk is milk produced under exceptionally exacting conditions of sanitation and cleanliness and which therefore contains a very low original bacteria count. It may be marketed either in a raw or a pasteurized state.

Vitamin D milk is milk the vitamin D content of which has been increased to approved levels either by irradiation of the milk with ultraviolet light which transforms the cholesterol compounds of the milk into the cholesterol type of vitamin D; by feeding cows irradiated yeast which contains ergosterol and thus yields the ergosterol type of vitamin D; or by adding vitamin D directly to the milk.

CONCENTRATED MILKS

It has been seen that fresh fluid milk has a relatively low solids content. The large bulk occupied by water in milk is frequently considered

a disadvantage which can be overcome by modern methods of evaporation which remove part, or a greater proportion, of the water, leaving a product containing a high concentration of milk solids. If only a part of the water is removed the resultant product is evaporated or condensed milk. If practically all the water is removed, dry milks are obtained. Improvements in methods of evaporation have been such in recent years that this treatment does not markedly affect the original characteristics of the milk solids. Greater uniformity of composition, easier handling, and improved keeping quality are some of the advantages of concentrated milks.

The process of condensing milks involves essentially preheating the milk to higher than pasteurization temperatures in "hot-wells" which are steam jacketed kettles usually made of stainless steel, and then passing the heated milk into a vacuum pan where evaporation of the water portion of the milk is greatly facilitated by a reduction in the atmospheric pressure. The purpose of preheating is two-fold: a thorough pasteurization of the product is obtained and burning of the milk is prevented on the heating surfaces of the vacuum pan. The vacuum pan consists of a relatively large closed retort made of stainless steel and equipped with heating coils and a vacuum pump which permits the creation of a vacuum of 24 to 28 inches of mercury (compared with 30 inches of normal atmospheric pressure). The boiling point of milk at atmospheric pressure is 212.3° F., or slightly higher than that of pure water. As the boiling point of a solution is raised by an increase in its concentration, higher temperatures still would be required to obtain adequate concentration of the milk. Under such conditions the milk would become overheated and yield an unsatisfactory product. With the vacuum normally used in the production of condensed milks, evaporation proceeds within a temperature range of 120° to 140° F., which is well within the safe zone.

Condensed or evaporated milks are available to the baker in a variety of types. When fluid whole milk is subjected to the evaporation process, the resultant product is known as evaporated milk which is defined by the Food and Drug Administration as sweet whole cow's milk evaporated so that it contains not less than 7.9 percent by weight of milk fat and 25.9 percent of total milk solids. The average water content of evaporated milk is 72 to 75 percent. Because the product is highly perishable, it must be hermetically sealed in a metal container and sterilized at a temperature of 240° to 245° F. Evaporated milk usually contains small amounts of stabilizers (not exceeding 0.01 percent) in the form of disodium phosphate or sodium citrate or both, to ensure smoothness.

Plain condensed milk is produced similarly as evaporated milk except

that its water content is reduced to a lower level than is the case with evaporated milk. It is generally sold in bulk to bakeries. Since this type of processed milk need not be sterilized, nor packed in hermetically · sealed containers, its use is advocated only when frequent deliveries can be made and the milk is used up rapidly.

In addition to regular evaporated and condensed milks, evaporated and condensed separated or skimmed milks are available to bakers. These milks differ from the regular milks by having practically their entire fat content removed as cream prior to their processing. They are frequently made to contain specified percentages of nonfat solids to meet certain requirements of users. Special treatment of condensed separated milk with high pressure live steam in the vacuum pan results in the so-called "superheated milk" which is especially designed for bakery use.

Sweetened condensed milk is obtained when sugar or dextrose or both are added to the fresh fluid milk prior to its evaporation. It is defined as the liquid or semiliquid food made by evaporating a mixture of sweet milk and refined sugar (sucrose) or any combination of refined sucrose or the corn sugar dextrose to such a point that the finished sweetened product contains not less than 28 percent of total milk solids and not less than 8.5 percent of milk fat. A typical sweetened condensed milk will contain 8.5 percent fat, 8.1 percent protein, 54.7 percent sugar (including lactose), 1.7 percent ash, and 27 percent water.

Sweetened condensed separated milk differs from sweetened condensed milk only in its fat content, which is reduced to the lowest practical point by cream separation from the original fluid milk. The occasional occurrence of "sandiness" or "grittiness" in the sweetened condensed milks is due to too rapid cooling of the evaporated product from the vacuum pan which leads to the formation of lactose crystals large enough to be felt on the tongue and palate. The sweetened milks are not heat sterilized subsequent to their evaporation since their high sugar content imparts to them sufficient keeping quality to prevent spoilage for adequately long periods. They are supplied to bakeries in bulk or in smaller sized containers.

DRY MILKS

One of the major developments in American baking technology came with the commercial development of nonfat dry milk solids, which is the product obtained by the complete drying of separated milk. Not only is this product a valuable baking ingredient which improves both the nutritional value and general physical quality of bakery products, but it also affords the best economic utilization of the tremendous volume of skimmed milk which formerly represented a by-product of dairy processing. The

manufacture of dry milks, of which nonfat dry milk constitutes the major portion, is today a major industry. A bulletin of the American Dry Milk Institute (*284*) points out that in 1916 there were produced in the United States some 16.5 million pounds of nonfat dry milk and a little over 2 million pounds of dry whole milk. By 1950, the production for human consumption of nonfat dry milk solids has increased to 845 million pounds and that of dry whole milk to 129 million pounds. Total production of dry buttermilk in 1946 was 45 million pounds. The principal user of nonfat dry milk solids is the commercial baker.

The general category of dry milks includes several types which are differentiated principally in accordance with their fat content. If whole

Fig. 46—Microphotograph of nonfat dry milk solids produced by the spray process. (*Courtesy American Dry Milk Institute, Inc.*)

milk, containing all of the original butter fat, is dried, the product is known as dry whole milk. If the milk is separated only partially, it will yield partially defatted dry milk. If practically all of the butter fat is removed from the original fluid milk, then the dry product is known as nonfat dry milk solids. Partially defatted milk is generally produced for special purposes and is little used by commercial bakers.

Dry milks are produced by either one of two methods, namely spray drying or roller drying. In the spray process, milk is drawn from a holding tank into a preheating tank where its temperature is raised to 180° F. for 30 minutes. It is then pumped into a concentrating chamber, also called liquid collector, where the heated milk is subjected to repeated aeration at an elevated temperature, the hot air used for this purpose being obtained as exhaust air from the main spray drying chamber. In this process, the milk loses a considerable portion of its water content so that a rather highly concentrated product is obtained. This pre-

condensed milk is then pumped at high pressure into the drying chamber through a needle point orifice which atomizes the milk into a fine mist. The mist is met by a blast of hot sterilized air which dries the sprayed milk almost instantaneously. The dry milk drops to the bottom of the drying chamber from whence it is removed continuously and automatically. A number of variations in the individual processing steps of spray drying are encountered in practice. Thus the concentrating chamber may be replaced by a regular vacuum pan for pre-condensing the milk. The milk spray within the drying chamber may be created either by pressure atomizers or by centrifugal force. In the latter method, the milk flows in a steady stream onto the surface of a disc revolving at

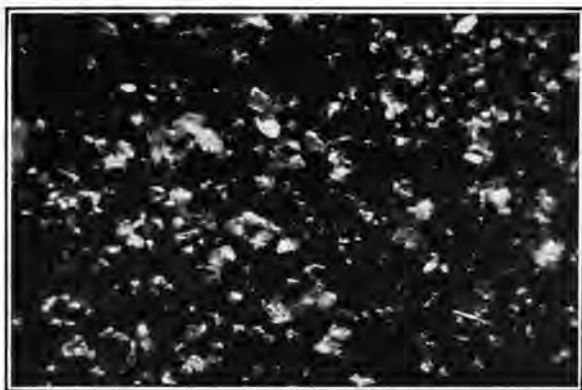FIG. 47—Microphotograph of nonfat dry milk solids made by the atmospheric roller process. (*Courtesy American Dry Milk Institute, Inc.*)

extremely high speed which atomizes the liquid. The drying chamber, in which the final removal of moisture occurs, may be either conical, cylindrical, square or rectangular in shape and of variable size. Collector systems for the recovery of milk particles carried along by the exhaust air from the drying chamber are also of various design.

In the roller process use is made of a pair of steam heated rolls or drums upon which the milk is dried in thin uniform layers and subsequently removed by stationary knives fitted to the rollers. Milk intended for roller-drying does not require pre-condensing, although it is preheated and pasteurized. The preheated milk is fed into the reservoir formed by the closely set rolls which, revolving in opposite directions, pick up a thin film of the milk and dry it. This dried milk is then removed by the knives in the form of large thin sheets and conveyed to a flaker or hammer mill which reduces it to the desired fineness.

A variation of the roller process, in which the rolls are enclosed in a

vacuum chamber, is also used to a limited extent. The maintenance of a partial vacuum during drying operations permits the use of lower temperatures and results in a product which closely resembles the spray dried product in solubility, color, flavor, and hygroscopic property.

The practice of preheating the milk prior to drying is essential to good baking quality of the milk. Research has shown that if the preheat treatment is omitted or improperly carried out, a dry milk of poor baking quality is obtained. While the exact change in milk produced by the heat treatment is not as yet fully understood, it has been found that the factor responsible for the poor baking quality of inadequately heated milk is in the serum protein fraction of the milk.

Fig. 48—Microphotograph of nonfat dry milk solids made by the vacuum roller process. (*Courtesy American Dry Milk Institute, Inc.*)

The effects of unheated milk are in the nature of decreased volume and slacker dough consistency similar to that obtained by the addition of small quantities of cysteine and glutathione. This has led Stamberg and Bailey (*285*) to suggest that the dough softening action of raw milk is caused by the sulfhydryl groups of cysteine present in the milk and that upon heat treatment these groups are either oxidized to more stable disulfide linkages or otherwise modified. Larsen, Jenness and Geddes (*286*) have confirmed the observations of previous investigators and were able to localize the dough-softening milk constituents in the milk serum proteins which constitute about 7.5 percent of nonfat milk solids. Their work appears to indicate that heat denaturation of the serum proteins is the basic reaction involved in eliminating their undesirable effect. They suggest that protein denaturation may cause a molecular rearrangement in which many of the sulfhydryl groups of cysteine become less available for reaction.

The following table gives the range of composition of various dry milk products (*276*).

TABLE 95.   RANGE OF COMPOSITION OF DRY MILK PRODUCTS
(Percentages)

Products	Water	Fat	Protein	Lactose	Ash
Dry whole milk........	2.4-4.5	25.0-29.2	24.6-28.3	31.4-39.9	5.6-6.2
Partially defatted dry milk...............	2.1-5.3	13.0-22.0	25.7-38.4	34.7-48.9	5.7-7.3
Nonfat dry milk solids..	2.71-3.62	0.78-1.03	35.6-38.0	50.1-52.3	8.00-8.36

THE GRADING OF NONFAT DRY MILK SOLIDS

Standards for several grades of nonfat dry milk solids were first established by the dry milk industry in 1929. These standards have been subsequently modified and at present apply to the grades designated as suitable for human consumption. The requirements of these grades are as follows (*284*):

GENERAL REQUIREMENTS FOR ALL GRADES

1. All nonfat dry milk solids for human consumption shall conform in all respects to Federal and State government regulations in force at the present time or that may be subsequently issued from time to time.

2. The factory and factory equipment used in the manufacture of nonfat dry milk solids shall be maintained in a strictly sanitary condition. No person or persons affected with any infectious, contagious or communicable disease, or who resides, boards or lodges in a household in which there is a person affected with such disease, shall be employed or permitted to work in or about any part of the factory in which nonfat dry milk solids is manufactured.

3. Nonfat dry milk solids shall be made from fresh, sweet milk to which no preservative, alkali, neutralizing agent or other chemical has been added and which has been pasteurized in the liquid state either before or during the process of manufacture at a temperature of 143° F. for 30 minutes or its equivalent in bacterial destruction.

4. Nonfat dry milk solids shall be reasonably uniform in composition. The color shall be white or light cream and free from a brown or yellow color typical of overheated stock and free from any other unnatural color. It shall be substantially free from brown specks.

5. The flavor and odor of nonfat dry milk solids in dry form or on reconstitution shall be sweet and clean and entirely free from rancid, tallowy, fishy, cheesy, soapy or other equally objectionable flavors or odors.

6. Nonfat dry milk solids shall be packed in substantial containers suitable to protect and preserve the contents without significant impairment of quality with respect to sanitation, contamination and moisture content under various customary conditions of handling, transportation and storage.

7. Nonfat dry milk solids shall be free from extraneous matter as described under Section 402(a) of the Federal Food, Drug and Cosmetic Act.

Extra Grade is so designated to indicate the highest quality of nonfat dry milk solids and, in addition to the foregoing General Requirements, shall meet the following specifications:

TABLE 96. SPECIFIC REQUIREMENTS FOR EXTRA GRADE NON-FAT DRY MILK SOLIDS

	Spray Not Greater Than	Vacuum Drum Not Greater Than	Atmospheric Roller Not Greater Than
Butterfat....................	1.25%	1.25%	1.25%
Moisture....................	4.00%	4.00%	4.00%
Titratable acidity (reliquified basis).....................	.15%	.15%	.15%
Bacterial count (reliquified basis)....................	100,000 per gm.	100,000 per gm.	100,000 per gm.
Sediment (reliquified basis)....	No. 3	No. 3	No. 3
Solubility index.............	1.25 ml.	2.00 ml.	15.00 ml.

Extra Grade nonfat dry milk solids shall be entirely free from hard lumps. The dry sample as well as the reliquefied sample shall be entirely free from any storage or scorched flavor or odor.

Standard Grade includes all nonfat dry milk solids that fails in one or more particulars to meet the requirements of Extra Grade but it must meet or come within the following requirements:

TABLE 97. SPECIFIC REQUIREMENTS FOR STANDARD GRADE NON-FAT DRY MILK SOLIDS

	Spray Not Greater Than	Vacuum Drum Not Greater Than	Atmospheric Roller Not Greater Than
Butterfat....................	1.50%	1.50%	1.50%
Moisture....................	5.00%	5.00%	5.00%
Titratable acidity (reliquified basis).....................	.17%	.17%	.17%
Solubility index.............	2.00 ml	5.00 ml.	15.00 ml.
Bacterial count (reliquified basis)....................	300,000 per gm.	300,000 per gm.	300,000 per gm.
Sediment (reliquified basis)...	No. 4	No. 4	No. 4

Standard Grade nonfat dry milk solids shall be reasonably free from hard lumps but may have a slight storage or slightly scorched flavor or odor before and after reliquification.

Any nonfat dry milk solids failing to meet requirements for Standard Grade may be considered an ungraded product, provided that any nonfat dry milk solids having a flavor or odor or other characteristics indicative of decomposition or neutralization, or which fails to meet the General Requirements for nonfat dry milk solids, shall be termed "Unfit for Human Consumption."

KEEPING QUALITY

Dry milks possess a rather pronounced hygroscopic character, i.e., they readily absorb moisture from the atmosphere. Moisture contents in excess of 4-5 percent tend to reduce the keeping quality of the product appreciably. To avoid an undue increase in moisture, nonfat dry milk solids are usually packaged in slack barrels of 200 pounds capacity with moisture-proof double liners, or in moisture-proof bags of 100 pounds capacity. Dry whole milk as a rule is packaged in tin containers to exclude contact with air which, during packaging, is evacuated and replaced by an inert gas, usually nitrogen. This is done to retard or prevent deterioration due to oxidation of the milk fat by atmospheric oxygen.

Dry milks may acquire certain off-flavors either in production or upon storage. The most frequently encountered off-flavor imparted to milk in production is the so-called "cooked" or "burned" flavor which results from subjecting the milk to high temperatures or long periods of heating prior to actual drying.

Dry milks which have been stored under improper conditions are prone to acquire stale, rancid and tallowy flavors. Staleness in dry milks usually results from excessive moisture content and high storage temperatures. To avoid stale flavors, the moisture content should not be permitted to exceed 2.5 percent and the storage temperature should be kept below 75° F., according Holm (*287*). Rancid and tallowy flavors do not as a rule occur in nonfat dry milk solids but rather in dry whole milks since these defects are associated with fat deterioration. Rancidity results from the hydrolytic action of lipases present in raw milk and may be prevented by preheating the milk adequately before drying, thereby destroying the enzymes. Tallowy flavors and odors result from the autoxidation of the fat by atmospheric oxygen. For this reason dry whole milks should be packaged in air-tight containers under an atmosphere of nitrogen or carbon dioxide. Oxidation is also accelerated by certain metal catalysts, chiefly copper and iron. The use of stainless steel equipment in the processing of dry whole milk is therefore an important requirement. The rate of oxidation is also markedly affected by temperature, the rate practically doubling with each increase of 10° C. (18° F.) (*287*). It is therefore important to store dry whole milk at temperatures not exceeding ordinary room temperature even when the product is packaged in an inert atmosphere of low oxygen content. Once the product is exposed to normal atmosphere, low temperature storage is recommended.

The storage period for which dry milk products may be safely kept varies considerably with the inherent keeping quality of the products and the storage conditions. Assuming that the dry milks have been pro-

duced under optimum conditions and that the storage temperature does not exceed 75° F., such products will normally remain usable for a period of six months. Milks of good initial quality and packaged in an inert atmosphere of low oxygen content may be kept for as long as one year without spoilage, if the storage temperature does not exceed 75° F.

EFFECTS OF NONFAT DRY MILK SOLIDS ON DOUGHS AND BREAD

The addition of nonfat dry milk solids to the dough in the generally recommended amount of 6 percent based on flour weight produces certain changes in the physical properties of the dough and in the quality characteristics of the resultant bread. These changes, which may be readily observed by an experienced baker under practical plant conditions, have been subjected to extensive studies by baking chemists and the results recorded in the literature.

Investigations into the effects of milk solids have shown that they affect the absorption, mixing requirements, fermentation rate, bromate requirements of flours, the baking temperature and the physical character of bread. Stamberg (*288*) points out that a superior dry milk usually requires an increase in absorption equivalent to the amount used and some powders have even higher absorptions. Therefore, if 6 percent of dry nonfat milk solids is used, the absorption is increased 6 percent or more over that of milk-free doughs. The high absorption of milk solids of superior baking quality is of importance in relation to cost since the increased bread yield largely offsets the extra cost of this ingredient.

Skovholt and Bailey (*289*), investigating the effect of milk solids on fermentation reactions, observed that while they have no measurable effect on the proteolytic activity in doughs they do reduce diastatic activity largely because they induce a lowering of the hydrogen ion concentration. This reduction in hydrogen ion concentration is attributable to the relatively high buffer capacity of the milk which prevents the normal decrease of the pH which occurs in fermenting water doughs. Brouilett and McDuffee (*290*) have reported that milk-free doughs will show an average pH value of 5.8 upon mixing which, after fermentation for 45 minutes, decreases to an average value of 5.1. Doughs containing milk, on the other hand, will have an average pH of 5.94 on mixing and of 5.72 after fermentation for the same period. Thus in milk doughs the change in pH amounts to only 0.22, whereas in milk-free doughs the change is 0.7. Since the optimum pH value for amylolytic activity is 4.7, diastatic action is favored in a water dough as against a milk dough. This retardation of amylolytic activity makes itself felt in a reduction of gassing power in sugar deficient doughs made from commercial flours. Hence

the addition of diastatic malt will generally be advantageous. If sufficient sugar is available in the dough, milk solids will cause an accelerated gas production since they apparently stimulate the zymase complex of yeast to greater activity.

Ofelt and Larmour (*291*) examined a series of flours, including representative types commonly used in commercial baking, with respect to the effects of potassium bromate and nonfat dry milk solids on their baking behavior. They found that in general the inclusion of 6 percent nonfat dry milk solids greatly increased the tolerance of flour toward bromate and tended to prevent the deleterious effects produced by excessive bromate treatment upon loaf volume and grain and texture.

This buffering effect is of considerable importance in practice since it affords some safeguard against the possibility of damaging flours which are already near their optimum oxidation condition, either through bleaching or through the addition of other oxidizing agents. Dry milk solids, together with appropriate amounts of bromate (in increments ranging from 0.001 to 0.004 percent depending upon the protein content of the flour) produced increases in bread volumes and improvements in texture which exceeded those obtained by optimum bromate treatment alone.

In certain flours, especially of the low-strength kind, nonfat dry milk solids alone produced greater improvements than could be obtained with the optimum dosage of bromate. Eisenberg (*292*) and Harris and Bayfield (*172*), the latter in studying the comparative effects of bleaching agents and potassium bromate in the presence of nonfat dry milk solids, confirmed the observation of Ofelt and Larmour that nonfat dry milk solids conferred a certain degree of tolerance toward potassium bromate, increasing the bromate requirement. They also observed that nonfat dry milk solids used in an amount of 6 percent increased the loaf volume and improved the grain and texture, crust color, and break and shred of the finished loaves. The bread improving action of milk was studied by Bohn and Bailey (*293*) who found that nonfat dry milk solids, when of good quality and when used at a 6 percent level in bread, produced an improvement in the volume, grain, texture, and the eating and keeping qualities of the bread. The degree of improvement in these quality factors decreased with a decrease in the quality of dry milk until "poor quality" dry milk had a deleterious effect upon bread characteristics.

PRACTICAL MANAGEMENT OF MILK SOLIDS IN BREAD PRODUCTION

Milk in fluid form, whether fresh or evaporated, is a rather highly perishable product which requires special precautions during storage if

serious losses through quality deterioration are to be avoided. The only safe method for preserving fresh fluid milk for any extended period of time is to keep it under refrigeration. Evaporated whole milk, when delivered in sealed cans, may be held for prolonged periods if the storage temperature is maintained at or below 70° F. Open cans from which a portion of the contents have been used must be placed under refrigeration to avoid rapid deterioration. Evaporated milks supplied in barrels are preferably kept at refrigerator temperatures if not used immediately. Sweetened condensed milks, while possessing a relatively high degree of inherent stability due to their high sugar content, require nonetheless some care in storage since under conditions of high temperature the sweetened milk products may be subject to fermentation. Prolonged storage may also lead to some crystallization of the sugar, imparting to the product a gritty taste. Milks showing crystal formation require thorough stirring prior to their use. Dry milks should be kept in cool, dry storage. Since dry milks are highly hygroscopic products, they readily absorb moisture from the atmosphere upon exposure to the air. For this reason dry milks are packaged in moisture-proof containers or in barrels provided with moisture-resistant liners. If the moisture content of the dry milk is permitted to exceed 5 percent, deteriorative changes proceed at a rapid rate. The milk will form lumps which are difficult to dissolve, and will acquire unsightly discolorations and unpleasant odors and flavors.

In adding dry milks to the dough in the mixer, the recommended procedure is to place the milk on top of the flour just prior to the start of mixing. This method prevents the undesirable formation of lumps which may occur when dry milk is put into the mixer in direct contact with the water. The lumps formed under the latter condition often fail to disperse during the mixing operation and give rise to spotty crusts on the finished loaves. Some bakers prefer to reconstitute the milk prior to its use in the dough. There is no apparent advantage to reconstitution and bakery technicians on the whole recommend the addition of milk in its dry form.

The introduction of high speed mixers, while resulting in improved bread qualities, has also greatly reduced the critical mixing period over which acceptable bread can be obtained. Thus, while mixing periods of 20 to 40 minutes were the rule with the earlier slow speed mixers, present day mixing times seldom exceed 15 minutes and optimum mixing is usually attained within an even shorter period. The mixing time has thus become a much more critical factor than it was formerly. Experimental studies by Stamberg and Bailey (*294*) have shown that doughs to which 6 percent nonfat dry milk solids has been added require a longer mixing time than do milk-free doughs, so that the effect of the milk solids is to increase the strength of flour. Practical experience also indicates

that doughs containing milk should be turned out somewhat slacker since they tend to tighten up during fermentation due to the progressive hydration of the milk solids. Given a high grade of nonfat dry milk solids, a good rule is to increase the absorption by an amount equal to the amount of dry milk used.

Nonfat dry milk solids have been shown to increase the fermentation tolerance of a dough and, when compared with milk-free doughs under identical conditions, to also lengthen the fermentation time somewhat. Whereas the fermentation time is readily controlled by the baker, fermentation tolerance, which covers that period of active fermentation during which bread of acceptable quality will result, is a far more critical factor. A short fermentation tolerance is largely responsible for the pronounced variation which may occur in the characteristics of bread produced from the same dough. Nonfat dry milk solids, by extending the fermentation tolerance, acts to stabilize the dough and therefore contributes materially toward the day to day uniformity of a bakery's bread.

Whether or not to include milk in sponges depends upon a variety of factors. As a very general rule, some or all of the nonfat dry milk solids may be added at the sponge stage if (a) a low protein or weak flour is used, (b) if the flour possesses an excess of amylolytic activity, (c) if the flour has a very short fermentation period, and (d) if the flour tends to break down easily. Nonfat dry milk solids should not be used in sponges if the reverse of the above factors is encountered, i.e., if a high protein, strong flour is used, if the flour lacks in amylolytic activity, if it requires a long fermentation period, or if it is difficult to condition.

Doughs containing 6 percent nonfat dry milk solids generally require a somewhat longer recovery period in the proofer and after coming from the rounder than do milk-free doughs. As a rule an extension of 2 to 3 minutes will prove adequate. Proper recovery of the dough pieces is essential if uniformly moulded loaves are to result. The final pan-proof of milk doughs is also slightly protracted as compared to water doughs. The proof box temperature should not exceed 95° F. and the relative humidity should be maintained slightly lower than is the case with milk-free doughs.

The matter of correct baking time is of some importance since the usual tendency for bakers is to underbake bread containing milk. This is due partly to a desire to obtain a bread possessing a soft crumb and partly to the more rapid coloration of the crust of milk bread. If baking time is adjusted solely on the basis of the degree of crust color formation, then breads containing normal amounts of milk solids will tend to be under baked. The milk sugar, lactose, is unfermentable by yeast and will hence be found in its original amount in the pan-proofed dough piece.

Color formation during baking is due to a combination of dextrinization, caramelization and melanoidin formation. Melanoidins, the principal coloring substances of bread crust, are formed by a reaction between sugars and amino acids, under the influence of heat. Doughs containing high amounts of residual sugar, such as milk containing doughs or young doughs, will therefore color more rapidly than will doughs in which very little residual sugar is present, such as old doughs or milk-free doughs. Every practical baker has observed this. In high sugar doughs, regardless of the source of sugar, the degree of crust coloration cannot therefore be taken as an indication of the degree of baking. As a general rule, milk-doughs must be baked to a deeper color than milk-free doughs to yield well-baked bread. In most cases a baking time, with properly adjusted baking temperature, of less than 30 minutes for 1 pound loaves will prove inadequate.

Milk has long been recognized as a bread improving ingredient, from the standpoint of both the nutritive value of bread and the physical characteristics of bread. The recommended addition of 6 percent of dry whole milk solids based on flour is based upon the fact that such an addition will yield a bread which is equivalent to a product in which all the liquid added is milk. In the case of nonfat dry milk solids, the product is equivalent to one obtained by the use of defatted liquid milk. The significance of dry milk additions to bread has been judged by the National Research Council (*295*) as follows:

"There is no need to discuss the wealth of experimental evidence showing the value of milk additions to bread. The nonfat solids commonly used contribute importantly to the quality of the protein mixture and they increase the quantity of the protein as well. Calcium, riboflavin and all the other important nutritional substances supplied by nonfat milk solids likewise are increased in direct proportion to the amounts of milk used. Feeding experiments with bread made according to commercial formulas repeatedly have demonstrated the superiority of bread made with milk over bread not so made.

"From the point of view of the effect of milk on the technology of bread production it may be mentioned that there is convincing evidence that the finished loaf of bread is in every measurable way a more palatable loaf when it contains milk. The crust of the loaf has a more agreeable color, the inside of the loaf or crumb, a softer texture and the entire loaf has a better shape. The bread tends to retain its moisture more tenaciously and so remain fresh longer. Toast made from bread containing milk is considered to be superior in flavor. It has also been shown experimentally that consumers prefer bread made with milk over bread containing no milk."

While the general recommendation has been to include 6 percent of non-fat dry milk solids for commercial bread, and up to 12 percent for institutional bread, Brouilett suggested the use of 8 percent nonfat dry milk sol-

STRAIGHT DOUGH FORMULA

	Lbs.	Ozs.
Flour	100	
Water	70	
Yeast	2	4
Yeast food		4-5
Malt		12
Salt	2	4
Sugar	5	4
Nonfat dry milk solids	8	
Shortening	5	

Procedure: The dough should be mixed on the firm side. In average well-controlled plants a fermentation time of 3 to 3½ hours will be required. Punching the dough is omitted, the dough being fed directly to the divider. Overhead proof should be as long as possible —12 to 15 minutes.

SPONGE-DOUGH FORMULA

	Sponge		Dough	
	Lbs.	Ozs.	Lbs.	Ozs.
Flour	60-65		40-35	
Water	37-40		31-28	
Yeast	2	4		
Yeast food		5		
Malt		8		
Salt			2	4
Sugar			5	4
Nonfat dry milk solids			8	
Shortening			5	

Procedure: The sponge can be mixed to suit individual plants. The sponge temperature is determined by both the temperature rise in the sponge and by the temperature at which the sponge is returned to the dough mixer, which should be within the range of 82–84° F. The rise in temperature of the sponge should be 8° to 12° F. If a 12° rise produces the best bread, then the sponge should be set at 70° F., i.e., 82° F. minus 12°. In high, dry altitudes the other extreme may be preferable. Under such conditions, with an 8° rise in sponge temperature, the sponge should be set at 74° F.

ids for commercial bread on the basis of test bakes in which bread containing no milk was compared with bread containing 4, 6 and 8 percent milk solids (*296*). With each type of bread, optimum mixing and fermentation conditions were determined experimentally so as to yield the

best possible bread characteristics. The water bread was employed as the comparative standard and an arbitrary numerical score of 100 assigned to it. On this basis the 4 percent nonfat dry milk addition yielded bread scoring 104, the 6 percent addition resulted in a score of 109, and the 8 percent addition gave the same score. If, however, both the sugar and the shortening called for by the formula of the 8 percent nonfat dry milk bread were increased by 1 percent each, a score of 111 was obtained. The straight dough and sponge-dough formulas yielding this superior bread, as given by Brouilett, are given on page 332.

Bread obtained by these formulas and methods is characterized by large volume, excellent grain and texture, and superior flavor.

CHAPTER XIII

EGGS AND EGG PRODUCTS

Eggs and egg products constitute important ingredients used by bakers principally in the production of cakes and sweet goods, in which products they comprise approximately one-half of the cost of the ingredients. In some cakes, such as sponge cake, the cost of eggs may amount to as much as 70 percent of the total ingredient cost.

Eggs are commercially available to the baker in four forms, namely shell eggs, liquid eggs, frozen eggs and dried eggs. The separated whites and yolks may also be had in liquid, frozen or dried form. Certain modified egg products, such as sugar yolks and glycerin yolks are also produced for use by the baking industry. Whereas in former years bakers used chiefly shell eggs, improved freezing methods and more careful selection of top grade eggs intended for freezing have resulted in an increased uniformity of the frozen product which has greatly enhanced its acceptability to the baker so that at the present time the use of frozen eggs by the baking industry exceeds by far that of shell eggs. Dried eggs, despite their advantages of exceptional keeping quality and convenient form, have failed at attain popularity with commercial bakers due chiefly to the adverse changes which occur in the egg material upon drying and which detract from the product's value as a cake ingredient. Dried eggs are an important ingredient in most prepared flour mixes, however.

STRUCTURE OF EGGS

Most readers are undoubtedly familiar with the general structure of eggs, though perhaps some of the finer structural details may have escaped their observation. The principal parts of an egg are the hard and brittle outer shell, the viscous translucent white, and the yellow yolk. There are, in addition, a number of membranes and less conspicuous parts. The yolk, in a normal new-laid egg of good quality, is nearly round, of uniform surface color and approximately centered in the egg. A small area, known as the germ spot, appears on the yolk surface, usually on the upper side as the egg is broken out. The yolk is enclosed in a sack called the vitelline membrane which maintains the yolk in its normal spherical shape.

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The yolk is suspended in the egg white or albumen which consists of several parts or layers of thin and thick white. A rope-like mass known as the chalaza at each end of the egg provides anchorage for the yolk in the white. Immediately surrounding the yolk is a thin layer of jelly-like albumen, followed by a layer of thick white. The outermost layer of albumen consists again of rather fluid white. The shell is lined by two membranes, namely the outer shell membrane which is next to the shell, and the inner shell membrane which is next to the egg liquids. These two

CROSS SECTION OF AN EGG

YOLK GERM

SHELL

YOLK MEMBRANE

INNER MEMBRANE

AIR CELL

CHALAZA

DENSE LAYER
OF ALBUMEN

OUTER MEMBRANE

JELLY-LIKE PORTION
OF ALBUMEN

WATERY PORTION
OF ALBUMEN
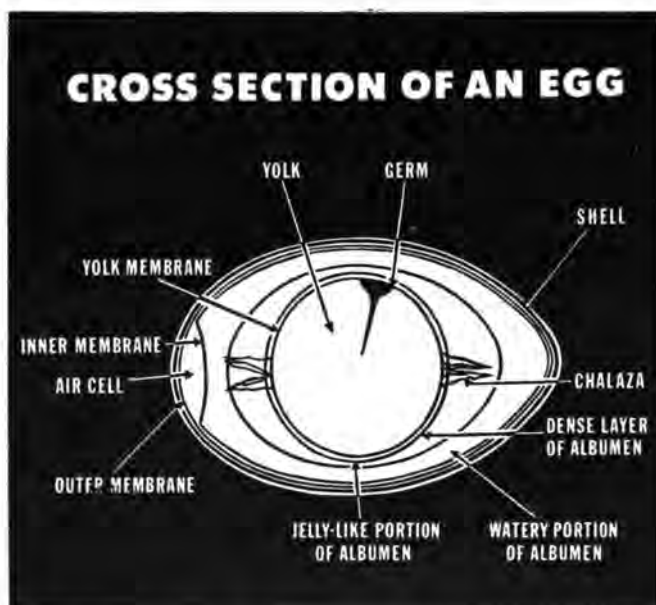
FIG. 49—Egg diagram showing the various components of an egg.

membranes usually adhere close to each other except at the large end of the egg where an air space or air cell forms between them as the egg cools and ages. The shell, which constitutes a protective container for the liquid parts of the egg is covered in the new-laid egg with a gelatinous coating which tends to seal the pores.

PHYSICAL COMPOSITION

Langworthy (*297*) has reported the average shell eggs as purchased to consist of 10.5 percent shell, 57.9 white, and 31.6 yolk. On the basis of the edible portion, eggs are composed of 64.6 percent white and 35.4 percent yolk. Eggs, however, may deviate considerably from these figures as is apparent from the following table (*298*):

TABLE 98. PHYSICAL COMPOSITION OF EGGS

Egg weight (grams)	Total contents		White			Yolk			Shell and membrane	
	Weight	Percent of egg weight	Weight	Percent of egg weight	Percent of weight of egg contents	Weight	Percent of egg weight	Percent of weight of egg contents	Weight	Percent of egg weight
	grams	percent	grams	percent	percent	grams	percent	percent	grams	percent
[1]55.6	50.0	89.9	31.4	56.5	62.8	18.6	33.4	37.2	5.6	10.1
[1]56.0	49.7	88.7	33.4	59.6	67.2	16.3	29.1	32.8	6.3	11.3
[2]56.7	51.4	90.7	33.1	58.4	64.4	18.3	32.3	35.6	5.3	9.3
[3]57.1	50.2	87.9	32.1	56.2	63.9	18.1	31.7	36.1	6.9	12.1
[4]56.3	50.3	89.3	32.5	57.7	64.6	17.8	31.7	35.4	6.0	10.7

[1] Average of several breeds.   [2] Rhode Island Red.   [3] Breed unknown.   [4] Average.

The observed variation in the physical composition of eggs is generally due to several factors, such as age, diet, breed, and inherited characteristics of the chicken. In eggs within the average weight range of 1.8 to 2.1 ounces, or 50 to 60 grams, the percentage composition of yolk and white is fairly constant, whereas in eggs either below or beyond that weight range the percentage of yolk tends to decrease and the percentage of white to increase.

In general, shell eggs, in quantities of 100 pounds, yield 10 to 12 pounds of shell, 58 to 60 pounds of white, and 30 to 32 pounds of yolk. The following table shows the quantities of each obtained from 100 eggs of the sizes indicated.

TABLE 99. QUANTITY OF EGG MATERIALS PRODUCED FROM 100 EGGS OF DIFFERENT SIZES[1]

Eggs per pound (number)	Liquid Eggs				Dried Eggs		
	Yolk	White	Whole egg	Shell	Yolk	White	Whole egg
	pounds	pounds	pounds	pounds	pounds	pounds	pounds
7	3.99	8.88	12.87	1.41	1.88	1.25	3.77
8	3.66	7.58	11.24	1.25	1.72	1.07	3.29
9	3.44	6.55	9.99	1.12	1.62	0.92	2.93
10	3.28	5.69	8.97	1.04	1.55	0.80	2.63
11	3.19	4.94	8.13	0.95	1.50	0.69	2.38

[1] The data are computed on the basis that 1 pound of dried egg is from 3.41 pounds of liquid whole egg, 7.12 pounds of liquid whites, or 2.12 pounds of liquid yolk.

CHEMICAL COMPOSITION

The chemical composition of normal eggs, in contrast to their physical composition, is remarkably constant, and the relatively minor variations

which have been reported are of no practical significance. The Department of Agriculture, on the basis of numerous analyses, gives the following average percentage values for total egg meats: water, 73 percent; protein 13.3; fat, 11.5; nitrogen-free extract, 1.1; free sugar as glucose, 0.3; ash, 1.0. The mineral constituents include mainly potassium, sodium, magnesium, calcium, sulfur, phosphorus, chlorine, in addition to traces of iron, aluminum, zinc, copper, lead, fluorine, iodine, silicon, arsenic, boron, chromium, rubidium, strontium, titanium, and vanadium.

With regard to egg white, considerable variations have been found in the proportion of fluid and firm white. In general, the outer fluid white will be found to comprise some 20 to 55 percent of the total white; the firm white some 27 to 56 percent; and the inner fluid white some 11 to 36 percent. It appears that the difference between firm and fluid white is due chiefly to a difference in mucin content, the ratio of mucin content of the firm white to the thin white being about 9 to 1. The egg white consists of five different proteins, of which albumin is by far the most important, constituting about 69.7 percent. The other proteins include conalbumin, 9.0 percent; globulin, 6.7 percent; mucoid, 12.7 percent; and mucin, 1.9 percent.

The principal constituents of egg white are water, 86 percent; protein, 11.6 percent; fat, 0.2 percent; nitrogen-free extract, 0.8 percent; free sugar as glucose, 0.4 percent; and ash, 0.8 percent.

In contrast to egg white, the yolk is considerably more diverse in composition. The average percentages of constituents have been reported as follows: moisture, 49.0; protein, 16.7; fat, 31.6; ash, 1.5. LeClerc and Bailey (*299*) give the following values for egg yolk: moisture 47.2 to 51.8 percent; ash, 0.33 to 1.0; fat, 20.3 to 22.8; lecithin, 7.2 to 10.7; vitellin, 15.6 to 15.8; nuclein, 1.5; cerebrin, 0.3; glycerophosphoric acid, 1.2; cholesterin, 0.44 to 1.75; glucose, 0.55; and coloring matter, 0.5.

A summary of the chemical composition of whole egg, yolk and white is given in Table 100 compiled from data reported by the Department of Agriculture.

From these values it is evident that the ash of the yolk differs materially from that of the white, being much richer in calcium, phosphorus, and iron, and poorer in sodium, potassium, chlorine and sulfur. It is also clearly shown that nearly all of the fatty materials of the egg are present in the yolk. This accounts largely for the lack of whipping quality in the yolk, aside from the fact that the yolk proteins also differ in character from the albumen of egg white, lacking the fibrous structure of the latter. The fat is present in the yolk in a finely emulsified state, some of it being combined with lecithin.

TABLE 100. AVERAGE CHEMICAL COMPOSITION OF EGGS

	Whole egg %	Yolk %	White %
Moisture	73.0	49.0	86.0
Protein	13.3	16.7	11.6
Fat	11.5	31.6	0.2
N-free extract	1.1	1.2	0.8
Sugar (as glucose)	0.3	0.21	0.4
Ash	1.0	1.5	0.8
Potassium	0.15	0.113	0.15
Sodium	0.16	0.049	0.16
Magnesium	0.01	0.017	0.011
Calcium	0.05	0.147	0.006
Iron	0.0027	0.0072	0.0002
Sulfur	0.23	0.2	0.212
Phosphorus	0.21	0.59	0.017
Chlorine	0.18	0.17	0.18

Also traces of aluminum, zinc, copper, lead, fluorine, iodine, silicon, arsenic, boron, chromium, rubidium, strontium, titanium, and vanadium.

BACTERIOLOGY OF EGGS

Eggs are a highly perishable food product and unless kept under proper conditions of sanitation and storage may in a relatively short time become inedible. Deterioration of egg quality is usually attributable to growth of bacteria and molds. Since the majority of eggs, as laid, are sterile or nearly so, heavy bacterial infection is an indication of improper handling and insanitary conditions.

Since incubating eggs are maintained for prolonged periods at temperatures which are near the optimum for growth of many spoilage organisms, it is evident that the egg must possess some protective devices against certain types of microorganisms if the majority of fertilized eggs are to hatch. Measurements have shown that the pH value of newly laid eggs is about 7.6. Loss of natural carbon dioxide, which at ordinary temperatures is almost complete in 24 hours, causes the pH value to rise to about 9.0, a level which is beyond the tolerance of many bacteria. Furthermore, egg white has been found to contain a germicidal factor, called lysozyme, which prevents the development of a number of types of microorganisms which gain access into the egg liquids. This protective substance, however, loses its potency as eggs are stored for prolonged periods so that the ultimate keeping quality of eggs is largely determined by storage conditions.

Shell eggs, to keep satisfactorily, must be stored dry and cool. In commercial storage, where eggs are to be held for 6 months or more, the

temperature is usually maintained at 29 to 31° F., which is just slightly above the freezing point of the egg liquids. In the bakery, shell eggs should be kept in the refrigerator at about 40° F., if they are not used immediately. At this temperature the growth of bacteria and molds is greatly retarded and the eggs can be safely held for several weeks.

Of almost equal importance to low temperature is keeping the eggs dry. An egg which has been wetted by washing or moisture condensation is much more subject to spoilage than an egg kept dry at all times. This is due to the fact that the egg shell possesses a porous structure with some of the larger pores traversing all layers of the shell. Water on the shell, by entering the larger pores, therefore supplies a suitable medium by which bacteria may find passage into the egg substance. Dirty shell eggs should therefore never be washed, except immediately prior to their use. High humidity conditions also affect the keeping quality of eggs adversely due to excessive mold growth.

The principal types of defective eggs found during and after storage are green white, digested whites, and white, red, and black rots, and musty eggs. As a rule these types of spoilage are accompanied by decided chemical decomposition and heavy bacterial infections. Frequently, spoilage is brought about by one bacterial or mold species, with other types of microorganisms being present as incidental adjuncts to the main infection. Species of *Pseudomonas* and *Achromobacter* have been shown to cause mustiness in eggs. Several types of bacteria cause rots. The odor known as "baker's must" which occurs in eggs which appear to be in good condition otherwise is produced by *Achromobacter perolans* (*300*). The odor is characteristic, very offensive and penetrating. One such egg will ruin a large batch and it is therefore good practice in the bakery to check each egg individually before adding to the egg mixture.

CANDLING OF EGGS

The quality of eggs is determined commercially by the so-called "candling" process which consists of holding the egg before a bright light in a dark room and looking through the shell. The candle is a rather simple device consisting of a bright light enclosed in a metal case which contains an opening just large enough to permit illumination of the whole egg. The operator or candler holds the egg against the light and gives it a quick twist on its long axis, observing the resultant motion and appearance of the yolk. When the egg is in good condition and possesses a normally thick white, the yolk moves only slightly away from the center when it is twirled. As an egg deteriorates in quality, the yolk, on the other hand, floats closer to the shell, moves more quickly, is no longer

situated in the center of the egg and become much more readily visible before the candle. Experienced candlers can detect these changes in fresh eggs which have been kept for about 5 hours at 100° F.

In addition to yolk position and mobility, the candler examines the egg for other signs of quality deterioration and defects. Thus the size of the air cell and the "tremulosity" of the air cell membrane are both generally used as indices of quality, an increase in the size of the air cell being interpreted as a sign of a decrease in the quality of the egg. Eggs which have been subjected to rough handling may show a tremulous or wavy air cell. This is caused by the shell membranes becoming separated over a wider area than is actually occupied by the air cell itself so that the air cell has a relatively greater freedom of movement. The edible quality of the egg is not affected by this condition.

A rather common defect found in eggs is the occurrence of blood spots on the yolk surface. These small blood clots usually represent minute blood vessel fragments which have become detached in the hen's ovary during egg formation. They are not of pathological origin and therefore do not detract from the actual edibility of the egg, although their occurrence definitely interferes with the salability of the eggs. Another blood condition, commonly known as a blood ring, arises when germ development has proceeded to a point where discrete blood lines have been formed. Upon the death of the developing embryo, this blood tends to contract into a ring about the germ spot. Such eggs are definitely classed as inedible. Blood may also be present diffused throughout the egg white, imparting to it a pale pink to blood-red coloration. The occurrence of such a condition also removes the egg from the edible class since it is caused by a hemorrhage in the hen's oviduct and is usually accompanied by heavy bacterial infection. Meat spots, or liver spots, representing small fragments of tissue of red or brown color, are occasionally found floating in the egg white. Their presence, except for detracting from the appearance of the egg, does not diminish its edibility. Most of these defects are detectable during candling and, if they are of a nature where the egg does not become inedible, reduce the grade classification of the egg.

The general character and condition of the white are judged in candling largely by the behavior of the yolk, on the basis that the firmer the white, or the greater the proportion of firm white, the less will be the movement of the yolk. Eggs containing firm whites are classed superior to eggs containing thin whites since egg white tends to become fluid with age. However, fluidity of egg white is not always a reliable index to age, since some hens consistently produce thin egg white, while others produce eggs having practically no thin white. Thus a freshly laid egg of the first

type may be judged stale, while a stale egg of the latter type may be judged fresh.

While candling is the only practicable method of evaluating the quality of whole eggs, several methods have been devised for measuring the quality of opened eggs. One is the determination of the yolk index which consists of measuring the height and width of the separated yolk.
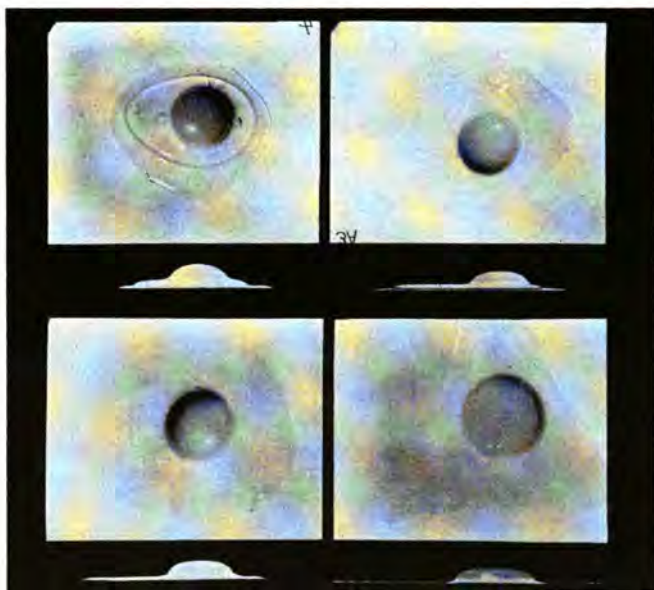

FIG. 50—Broken out eggs of different grades. High quality eggs have jelly-like white and high yolk (upper left), while low quality eggs have watery white and spread out yolk (lower right).

The yolk index is obtained by dividing the height of the yolk by its diameter. The more spherical the yolk, the greater will be the index value and the better the quality of the egg. Similar measurements carried out on thick white yields an "index of the thick white." Another method consists in determining the percentages of thick white and thin white. The higher the percentage of thick white, the better the eggs are considered to be. Still another method compares the opened eggs with a series of photographic charts, prepared by Van Wagenen of Cornell University, which also provides a system of quality scoring.

U. S. STANDARDS AND GRADES

The practice of classifying eggs according to their quality or grade, using the United States Standards as the basis, is becoming rather general in most parts of the country so that at nearly all the larger terminal

markets, Government-graded eggs may be purchased by the dealer or consumer. The graded eggs are packaged in cartons approved by the Agricultural Marketing Service, and the cartons sealed with certificates of quality, also approved by the Service, which show the grades of the eggs, their size and the date of candling. The specifications covering United States grades for individual shell eggs are given below.

SPECIFICATIONS FOR OFFICIAL UNITED STATES STANDARDS
FOR QUALITY OF INDIVIDUAL SHELL EGGS

(Effective January 2, 1943)

1. U. S. Standards for quality of individual shell eggs with clean unbroken shells shall be as follows:

   U. S. Grade AA. The shell must be clean, unbroken and normal. The air cell must not exceed $\frac{1}{8}$ inch in depth and may be regular or slightly wavy. The yolk outline must be free from defects or blemishes visible before the candle. The white must be clear and firm.

   U. S. Grade A. The shell must be clean, unbroken and normal. The air cell must not exceed $\frac{2}{8}$ inch in depth and may be regular or slightly wavy. The yolk outline may be fairly well defined. The yolk must be practically free from defects or blemishes visible before the candle. The white must be clear and reasonably firm.

   U. S. Grade B. The shell must be clean and unbroken, but may be slightly abnormal. The air cell must not exceed $\frac{3}{8}$ inch in depth and may show total movement not in excess of $\frac{3}{8}$ inch. If the air cell is small (not over $\frac{2}{8}$ inch in depth), it may be free. The yolk outline may be well defined. The yolk may show definite but not serious defects visible before the candle. The white must be clear but may be slightly weak.

   U. S. Grade C. The shell must be clean and unbroken but may be abnormal. The air cell may be over $\frac{3}{8}$ inch in depth, and may be bubbly or free. The yolk may be plainly visible, and appear dark. The yolk may show clearly visible germ development, but no blood due to such development. It may show other defects that do not render the egg inedible. The white may be weak and watery. Small meat spots or blood clots may be present.

2. U. S. Standards for quality of individual eggs with soiled, stained, or dirty shells shall be as follows:

   U. S. Light Dirty. Individual egg that has not more than one-eighth of the shell surface slightly stained, slightly soiled, or slightly dirty but without loose adhering dirt and of the interior quality of U. S. Grade B or better shall be classed as U. S. Light Dirty.

   U. S. Dirty. Individual egg with more than one-eighth of the shell surface stained, soiled, or dirty, or with less than one-eighth of the shell surface stained, soiled, or dirty to such an extent that it is more than slightly stained, slightly soiled, or slightly dirty, or any egg with slightly stained, slightly soiled, or slightly dirty shell and of the interior quality of U. S. Grade C shall be classed as U. S. Dirty.

3. U. S. Standards for quality of individual eggs with checked or cracked shells shall be as follows:

U. S. Check. Individual egg with either clean or dirty shell that has an open crack or break in the shell but with the shell membrane unbroken and with no leakage of the shell contents shall be classed as U. S. Check.

U. S. Leaker. Individual egg with either clean or dirty shell that has an open crack or break in the shell and shell membrane and with the contents exuding or free to exude through the shell shall be classed as U. S. Leaker.

FROZEN EGGS

The freezing of eggs, either whole or separated into white and yolk, was initiated some forty years ago as a secondary process to the shell egg industry in an effort to salvage eggs which, though of satisfactory quality, had imperfect shells and therefore did not qualify for shipment as shell eggs. During the early years of the frozen-egg industry, the breaking stock thus consisted largely of dirty, cracked, thin-shelled, weak-membraned and under-sized eggs. Initial progress of the industry was slow until, with the expansion of commercial baking, there developed a steady and growing demand for high quality frozen egg of uniform character which led to a phenomenal growth of the frozen-egg industry. Thus in 1921 some 46 million pounds of total frozen egg products were packed. By 1931, the pack had increased to 152 million pounds, by 1941 to over 237 million pounds and by 1947 to nearly 400 million pounds.

The commercial freezing of eggs is now carried on under strictest bacteriological and chemical control. The better packing plants confine their packing season to the cool spring months since eggs laid from February through May, because of their greater volume and firmness of their whites, are considered superior to those laid during the summer months. When frozen hard, such superior eggs can be held for almost indefinite periods without noticeable deterioration so that the frozen product is generally of a better quality than even fresh laid eggs obtainable during the warm season.

Frozen egg products are available in three forms, namely whole mixed eggs in which the yolks and whites are thoroughly mixed together, separated yolks and separated whites. Frozen yolks prepared for the baking industry usually contain added sugar and sometimes glycerin or salt. These substances are employed as anticoagulants to prevent the coagulation and dehydration of lecithoprotein during freezing which otherwise leads to poor emulsifying properties of the thawed-out yolk. Egg yolk consists of approximately one half water, the remaining half being made up of fat, protein, lecithin, and small quantities of other solids. As this mixture is chilled to about 28° F., water separates out and forms ice crystals before the yolk begins to solidify. As freezing continues, more ice crystal formation occurs, and at the same time small leatherlike

lumps of separated egg solids are formed. These lumps reduce the emulsifying power of the yolks and tend to cause yellow yolk specks in the finished product in which they are used. The addition of sugar, glycerin or salt lowers the freezing point of the water content of the yolks and thereby prevents its separation from the solids. As a result freezing occurs without break-down of the colloidal structure of the yolk. Generally, about 10 percent sugar is used in frozen yolks designed for bakery use.

Whole eggs, prior to freezing, are mixed in a churn to obtain a homogeneous mass and then passed through a filter to remove all shell particles, membranes and other materials. They are then filled into 10, 15 or 30 pound tin cans and put into the sharp-freezer in which temperatures of $-10°$ to $-15°$ F. are maintained. At these temperature levels, a 30-pound can requires approximately 60 to 72 hours for complete freezing. The frozen product is then transferred to a storage room maintained within the temperature range of $0°$ to $-5°$ F., where it is kept until withdrawal for delivery.

Frozen whole eggs should have a solids content of 24 to 28 percent. Lee (*301*) suggests the following approximate analysis of whole egg as suitable for calculation in the bakery:

Protein...............	13.3%
Fat..................	12.2
Minerals.............	1.0
Total..............	26.5%

The proportion of yolk and white in the frozen whole egg is given as 35-40 parts of yolk and 60-65 parts of white.

Frozen egg white, separated cleanly from the yolk, is treated along similar lines in the packing plant as is the whole egg. The solids content should be within 11 to 14 percent. An excessively high solids content indicates that old eggs have been frozen since shell eggs lose moisture upon prolonged storage which is reflected in a concentration of solids in the white. Frozen egg white contains approximately 11.9 percent protein, and 0.6 percent mineral matter, or a total of 12.5 solids.

Except for the addition of such substances as sugar, salt, or glycerin to act as anticoagulants, frozen egg yolks receive much the same mixing, screening and freezing treatment as do the other egg products. Commercial egg yolk generally contains varying amounts of egg white since it is practically impossible to separate all the white from the yolk under commercial conditions. However, the egg white content of frozen yolk should be kept to a minimum. When excessive amounts of egg white are permitted to adhere to the yolk, the product's moisture content will

tend to increase because of the much higher moisture content of the whites. According to Lee (*301*) frozen sugar-yolk has the following approximate composition: protein 14.3 percent, fat 24.0 percent, mineral matter, 1.1 percent, and sugar, 10 percent; making a total of 49.4 percent of solids.

In addition to the three types of egg products discussed above, several different proprietary egg preparations, containing varying proportions of egg white to yolk, and varying additions of glycerin, sugar, salt and acid, are available to bakers. These products represent certain improvements over the natural products for special baking purposes.

Eggs frozen at low temperatures and maintained at −10° F. or lower do not undergo decomposition due to microorganisms and may be kept for years. However, certain complex physical changes do take place. If the white is frozen quickly, the water will be reabsorbed on thawing and the product will revert to its original physical condition. Freezing at low temperatures, however, increases the proportions of thin egg white. If the frozen white is kept for 4 to 5 months, a coagulation of certain protein material of the albumen occurs, and on thawing, white fibers of mucin will be visible in the viscous portion of the egg white. Untreated egg yolk, when frozen at extremely low temperature, undergoes a more radical change from a physico-chemical standpoint. It does not revert to the original fluid state but becomes a gummy, rubbery mass, the extent of the change depending in part on the length of time in storage. The volume of the thawed product will be less than that of the original material, and the lecithin will have become chemically altered and thereby lose free phosphoric acid. Due to the formation of ice crystals, which removes water from the yolk, there is an appreciable concentration of the salt of the yolk.

HANDLING OF FROZEN EGGS

At present relatively few commercial bakeries possess sufficient low temperature storage capacity to permit them to store frozen eggs for prolonged periods of time. Frozen eggs require storage temperatures of −10° to −15° F. which are generally available only in commercial cold storage warehouses. For temporary storage not exceeding two months' duration a holding temperature of 0° F. will prove satisfactory. No attempt should be made at any time to hold frozen eggs in freezer storage at temperatures above 0° F.

Bakeries lacking low temperature storage facilities should schedule deliveries of frozen eggs as close to the time of their use as possible. The temperature of delivered eggs will generally be about 15° F. The eggs, before they can be used, must therefore be thawed out and mixed to se-

cure uniform consistency. Thawing may be done by one of two methods.
The cans may be either set in a temperate part of the plant and per-
mitted to defrost slowly, or they may be placed in special defroster tanks
of running water at 50° to 60° F. The second method is preferable for
several reasons. First it is the more rapid procedure. At room tempera-
ture of 70° to 80° F., a 30-pound can of frozen eggs will require from 18
to 24 hours for proper thawing, and a 10-pound can will ordinarily take
from 12 to 14 hours, whereas by the second method, the respective thaw-

FIG. 51—Running water bath for defrosting cans of frozen eggs.

ing times are reduced to 5-6 hours and to 2-3 hours. Furthermore,
whereas the first method of defrosting subjects the eggs near the outside
of the can to temperatures of 55° and 60° F. for 15 or more hours, de-
frosting in running cold water keeps the outside temperature down to
33° to 34° F. for 5 to 6 hours. In the former case the eggs may become
curdled; in the latter, they retain their smooth appearance, fresh flavor,
and superior baking quality. It is important that the contents of the
entire container should be thawed and thoroughly mixed before use.

Frozen eggs, once defrosted, are very perishable and must therefore
be stored in as cold a refrigerator as possible. However, they should not
be permitted to refreeze since every refreezing causes greater denatura-
tion and greater damage to their colloidal properties.

DRIED EGGS

The first patent on egg drying was issued in the United States in 1865. However, it was not until about thirty years later that the egg-drying industry began to expand. Despite the advantages which drying offered as a method of preserving eggs and as a means for reducing shipping costs and storage space, lack of proper bacteriological control and the use of low quality breaking stock prevented the industry from attaining any degree of commercial importance. By 1915, when cheaper Chinese dried egg products began to reach the United States in volume, the industry became dormant until about 1927, when egg-drying operations were again attempted. It was not until World War II that the egg-drying industry received a tremendous impetus and experienced a phenomenal expansion. Since a large proportion of the output was shipped overseas there was again a decline in production when hostilities ceased. However, the vast increase in the production of prepared flour mixes, in the formulation of many of which dried egg products form an important ingredient, promises to maintain egg drying operations at a fairly high level.

Dried egg production, very briefly considered, involves the breaking of high quality eggs, mixing their contents in a churn and screening to eliminate shell fragments and membranes. The mixed batch is then sprayed under high pressure into the drying chamber where the atomized mixture comes into contact with air heated to 160° to 170° F. which effects practically instant drying. The egg powder settles on the floor from which it is removed for cooling and packing into barrels.

While this process is applicable to both whole eggs and separated yolk, the whites, because of their viscous nature, require a different treatment. The separated whites, consisting of both thin and thick white, are first subjected to a fermentation lasting about 72 hours, the purpose of which is to impart to the whites a uniform consistency. This reduction in consistency is carried out because of the superior whipping qualities possessed by the thinner whites. The fermented whites, spread on shallow pans or trays, are then dried in steam-heated cabinet or tunnel dryers at relatively low temperatures ranging from 110° F. at the beginning to 140° F. toward the end of the drying period which lasts about 6 to 12 hours. Depending upon the depth of the whites in the trays, the drying period may extend as long as 40 hours. The material is then cooled and broken into flakes for packing. The product is known as flake or crystalline albumen because of its luster and sheen, although it is not actually a crystalline substance. Powdered albumen is obtained by grinding and screening the flake product.

Unfermented albumen in the flake or crystalline form is also produced, the thick portion of egg white being liquefied by means of mechanical

pumping and straining and by acid or enzyme hydrolysis. Also, increasing quantities of whites are being dried by spray methods from whites liquefied by acids or enzymes.

RECONSTITUTING DRIED EGGS

LeClerc and Bailey (*302*) recommend the following ratios of water to dried egg for reconstituting the product:

Dried whole egg. Use 1 part of dried egg to 3 parts of water by weight. Allow the mixture to stand 4 to 5 hours, or until normal liquid-egg consistency is obtained.

Dried yolk. In reconstituting this product, 2 to 3 parts of water are required for 1 part of yolk. Allow the mixture to stand 1 hour.

Unfermented albumen. Mixing 1 part of dried albumen and 6 to 7 parts of water will produce a product similar to fresh whites. Allow the mixture to stand 3 hours.

Fermented albumen. Add 1 part of dried albumen to 10 parts of water. Allow the product to stand 3 hours.

All reconstituted egg products should be used as soon as possible, as they are comparable to fresh eggs and are, therefore, highly perishable.

The same authors suggest a procedure for determining the practical value of reconstituted dried white. One ounce of unfermented white is mixed with 7 ounces of water, or $1\frac{1}{2}$ ounces of fermented white with 15 ounces of water, and the mixture allowed to stand for 3 hours. It is then beaten in a 10-quart mixer, the unfermented white for 2 minutes at second speed and 4 minutes at high speed, and the fermented white mixture $1\frac{1}{2}$ minutes at medium speed and $1\frac{1}{2}$ minutes at high speed. The behavior of the resultant foam serves as a basis for evaluating the quality of the dried whites. If after leveling the foam surface, the depth of the foam, as measured by a ruler or gauge, exceeds $6\frac{1}{2}$ inches, the dried whites are of good quality; if the depth is less than 6 inches, a poor grade is indicated. If a handful of the foam is broken and a clean break and firm structure are obtained, its quality is good. If a crackle is heard, the body will not hold up. A drip test may also be made to measure the stability of the foam body. A weighed amount of foam is placed in a funnel and the time required for the first drop of liquid to come through is recorded. A high quality product has little or no drip.

Watts and Elliott (*303*) have compared the backing characteristics of fermented flake albumen of Chinese origin, a commercial acid treated dried white, a white dried in the laboratory at 45° C. in a vacuum oven and fresh liquid white. They confirmed the previous observation that commercial dried whites whipped better and were hence more suitable for meringue mixtures than either fresh white or vacuum-dried white. The increased whipping ability of commercial whites is attributed to the

partial hydrolysis brought about by the fermentation or acid treatment given the material prior to drying. On the other hand, the commercial treated whites were greatly inferior to fresh or untreated dried whites in all batter and dough products, this inferiority being traced to the low pH and decreased amount of heat-coagulable protein of the commercial products. These investigators found the whipping test for foam volume and drainage described by LeClerc and Bailey (*299*) to be of little value for determining the suitability of the white for baking and suggest a pop-over baking test. In this test, sufficient batter, including all ingredients except the white, is prepared for all the samples of white to be tested. The basic formula is as follows:

All-purpose flour	100 g
Water	200 g
Egg yolk	34 g
Salt	2 g

To each 100 g. of smoothly mixed batter are added 30 g. of one of the dried whites to be tested, with a control using 30 g. of fresh white being run at the same time. After thorough mixing of the white, 20 g. portions of the completed batter are weighed into muffin tins and baked for 20 min. at 450° C. and another 20 minutes at 350° C.

USES OF EGGS IN BAKING

Generally speaking, good quality frozen eggs function very much like fresh liquid eggs and may be substituted for them on an equal par. Frozen eggs have the advantage that there is practically no waste in their use, whereas 3 to 4 percent of the whites may be lost in breaking shell eggs. Also, frozen eggs require less storage space. In frozen eggs, the yolks are firmer and the whites thicker than are the corresponding portions of stored shell eggs.

Woodroof (*304*) compared the baking quality of fresh and frozen eggs in three types of cakes, namely (a) angel food cake made with egg whites, (b) gold cakes made with egg yolks, and (c) butter cakes made with whole eggs. In the case of angel food cake, fresh egg whites gave slightly greater volume and a slightly finer texture. However, the cakes made with frozen egg whites were more moist and entirely acceptable. Gold cakes made with fresh egg yolks had the best color, but were not as light and tasty as those made with frozen yolks. Butter cakes made with frozen whole eggs containing 3 percent glycerin were superior in texture, volume, grain and were equal in other qualities to those made with plain frozen whole eggs and plain fresh whole eggs. From 1 to 3 percent salt in the frozen eggs markedly increased the flavor of gold and butter cakes.

Eggs are used in baking for the considerable contribution they make

to the nutritive value of the finished products and for the improvements they bring about in the volume, palatability, color and keeping quality of the baked goods in which they are used. When used in cake making, eggs exert a binding action; they are capable of leavening five to six times their weight of other ingredients; they possess considerable emulsifying power; the high fat content of the yolk imparts to eggs a marked shortening action; and they contribute to the flavoring of the baked product. The pleasing color which eggs impart to baked goods has long been accepted as an indication of quality. Eggs improve the cell structure of the product, maintaining it during the baking process, and reduce the evaporation of moisture from the baked product, thereby extending its fresh state. Frozen whole eggs are used in a variety of cake mixes, doughnut mixes, sweet doughs, jelly bases, cookies and pastries.

Egg yolks are used in cakes in which a rich yellow color is desired, and are often added to whole eggs in mixes to obtain a deeper color or greater emulsifying power.

Egg whites lend little flavor but produce a mellowing effect. They furnish thin but strong walls for tiny air cells formed when egg white is whipped. Even a small quantity of fat or egg yolk noticeably decreases the whipping quality of egg whites. Whites are used in making angel food cake, white pound cake, certain kinds of layer cake, box cakes, fruit cake, loaf cake, cup cake, cream icings, marshmallows, meringues, ice box cookies and other special products. In general, fresh or frozen whites are superior in foaming qualities to the average commercial dried white when used in combination with cream of tartar, calcium acid phosphate or other acid ingredient in making angel food cake.

LeClerc and Bailey (*299*) report on one important point in the use of egg white, both from fresh eggs and from eggs that had been stored for nine months. They observed that the thin portion can be whipped more readily to the proper consistency and thus makes a better cake than the more viscous albumen. When sufficient water is added to the thick white to reduce its viscosity to that of thin white, an improved angel food cake was obtained. Their experiments have shown that as much as a third of the white in an angel food cake formula can be replaced by water without affecting appreciably the quality of the cake.

Cake volume is to some degree controlled by the seasonal variations occurring in eggs. Thus spring laid eggs produce larger cake volumes than do summer laid eggs. In experiments on the use of eggs produced in April and July (*299*), is was found that sponge cakes made with April eggs were 15 percent larger than the cakes made with July eggs. Cream puffs made with April eggs also were larger and smoother than those made with July eggs.

CHAPTER XIV

WATER

Water occupies with flour, yeast and salt the position of a primary ingredient of dough. Without water the formation of a dough would be quite impossible and the amount of water used exerts a fundamental influence not only upon the character of the dough but also upon the quality of the finished product. Such dough properties as consistency, pliability, extensibility, stickiness—all of which are ultimately reflected in the general characteristics of the baked product—are either wholly or in part determined by the amount of water which is originally added to the flour during the mixing operation. The introduction of mechanical equipment into the bake shop has also brought in its wake the need for greater accuracy in determining the absorption capacity of flour so that the resultant dough will machine properly. Unless the liquid content of a dough is properly controlled, its handling properties will fail to meet the exacting requirements of automatic dough make-up equipment.

Pure water is a substance consisting of the elements hydrogen and oxygen with the chemical formula H_2O. Since water acts as a solvent for nearly all inorganic and organic substances, natural waters are never pure in the chemical sense and may be properly regarded as dilute solutions of salts in which small quantities of gases and organic matter are also dissolved. Both the amount and the nature of these impurities present in water may vary considerably with different localities and sources of supply. This is quite understandable when it is considered that each source of water has its own particular history. Generally speaking, natural water obtained from snow is the purest from a chemical standpoint since it is absolutely free of dissolved salts and contains a minimum of dissolved gases. Next comes rain water which is also free of salts but may contain appreciable quantities of dissolved gases derived from the atmosphere. Water which has run over soil, such as river and lake waters, or which has passed through various strata of earth, sand and porous rock, such as spring and well waters, contains varying amounts of both organic and inorganic impurities.

Waters are divided into two general categories according to source, namely surface waters and ground waters, terms which are self-explana-

tory.   Streams, ponds, lakes and impounded reservoirs constitute the principal sources of surface water, while springs, shallow wells and deep wells yield ground water.   The origin of water, i.e., whether from a surface source or a ground source, greatly influences its character.   Surface water, coming into contact with the surface soil and decaying vegetable matters, dissolves both mineral and organic substances and hence carries them along either in solution or in suspension as it collects in rivers, lakes, etc. It is also more extensively exposed to sources of bacterial contamination. Surface waters are therefore characterized by the presence of inorganic, organic and microbiological impurities, the extents of which are governed by individual local conditions.   Ground waters, on the other hand, are usually purified by their passage through layers of porous rock so that they are usually practically free from organic impurities.   However, in the course of its slow filtration through the rocks, the water has ample opportunity to add to its content of dissolved mineral matter so that ground waters as a rule are relatively high in mineral content.   The nature as well as the amount of the substances taken into solution by the water vary widely and depend upon the composition of the strata through which the water flows.

It is seen that different waters vary in their contents of both organic matter and dissolved mineral salts.   Depending upon the nature of the latter substances present, waters are classified into four categories, namely soft, hard, saline and alkaline.   The degree of hardness is expressed by a numerical value representing the dissolved hardness-forming minerals present in the water.   Because the actual amount of dissolved substances in average natural water is rather minute, the results of water analyses are usually expressed in parts per million (p.p.m.) rather than in percentages. One part per million equals 1/10,000 of 1 percent, or 0.0001 percent. Quantities at such concentrations are hence much more conveniently expressed as parts per million since this obviates the use of cumbersome figures.   This method of expressing the mineral content of water has become widely accepted and is now in general use.   An earlier method expressed dissolved substances in grains per gallon.   This proved less satisfactory since the U.S. gallon differs from the Imperial gallon, the unit of the British Empire, so that additional conversion factors were required to permit the interchange of values expressed by either system. Since 17.1 p.p.m. are equal to 1 grain per U.S. gallon, and 14.3 p.p.m. are equal to 1 grain per Imperial gallon, conversion from parts per million to grains per gallon or vice versa is a simple matter of multiplication or division.   To convert grains per U.S. gallon to grains per Imperial gallon, the factor 0.83 is used, while to convert grains per Imperial gallon to grains per U.S. gallon, the factor is 1.2.

THE SUBSTANCES OF NATURAL WATER

The following table lists the nature of the mineral constituents which commonly occur in natural waters:

TABLE 101. SUBSTANCES NORMALLY OCCURRING IN WATER (*305*)

Acids: Carbonic, sulfuric, hydrochloric, silicic, etc., usually in combination.
Aluminum: Oxide and sulfate.
Calcium: Carbonate, chloride, sulfate, nitrate, phosphate.
Iron: Carbonate, bicarbonate, oxide, sulfate.
Lithium: Carbonate, bicarbonate, sulfate, chloride.
Magnesium: Sulfate, carbonate, bicarbonate, nitrate, chloride.
Potassium: Carbonate, bicarbonate, chloride, sulfate and phosphate.
Silicon: Usually as silica or silicon dioxide.
Sodium: Chloride, carbonate, bicarbonate, nitrate, sulfate.

In addition to the more common minerals listed in the above table, natural waters may also contain traces of the salts of ammonium, antimony, arsenic, barium, boron, bromine, cadmium, caesium, chlorine, cobalt, copper, flourine, iodine, lead, rubidium, strontium, and zinc.

The map on p. 354 shows the average hardness of water supplied by municipal supply systems in over 600 cities of the United States. It will be noticed that only eight states, located in the Middle-West and the South-Western portion of the country, have what might be termed very hard water. Thirteen states, two in the North Pacific Coast area and the rest in the Atlantic Coast region and South-Eastern section, have extremely soft water. The remaining states have water ranging from soft to moderately hard. On a population basis, a greater proportion of people lives in the extremely soft to soft water area than in the hard water area (*306*). In interpreting the data presented in the map it should be kept in mind that these represent weighted averages and that considerable variations in water composition may occur within a given area.

WATER HARDNESS

Hardness in water is due almost wholly to the presence of calcium and magnesium ions. These are primarily responsible for the destruction of soap lather. Hence the hardness of a given water is determined by the dissolved amounts of such calcium salts as calcium bicarbonate $(Ca(HCO_3)_2)$, calcium sulfate or gypsum $(CaSO_4)$, calcium chloride $(CaCl_2)$ and calcium nitrate $(Ca(NO_3)_2)$, and such magnesium salts as magnesium chloride $(MgCl_2)$, magnesium bicarbonate $(Mg(HCO_3)_2)$, magnesium sulfate or Epsom salt $(MgSO_4)$, and magnesium nitrate $(Mg(NO_3)_2)$.

Degrees of hardness are usually calculated from the amount of a standard soap solution that must be added to a measured volume of water to
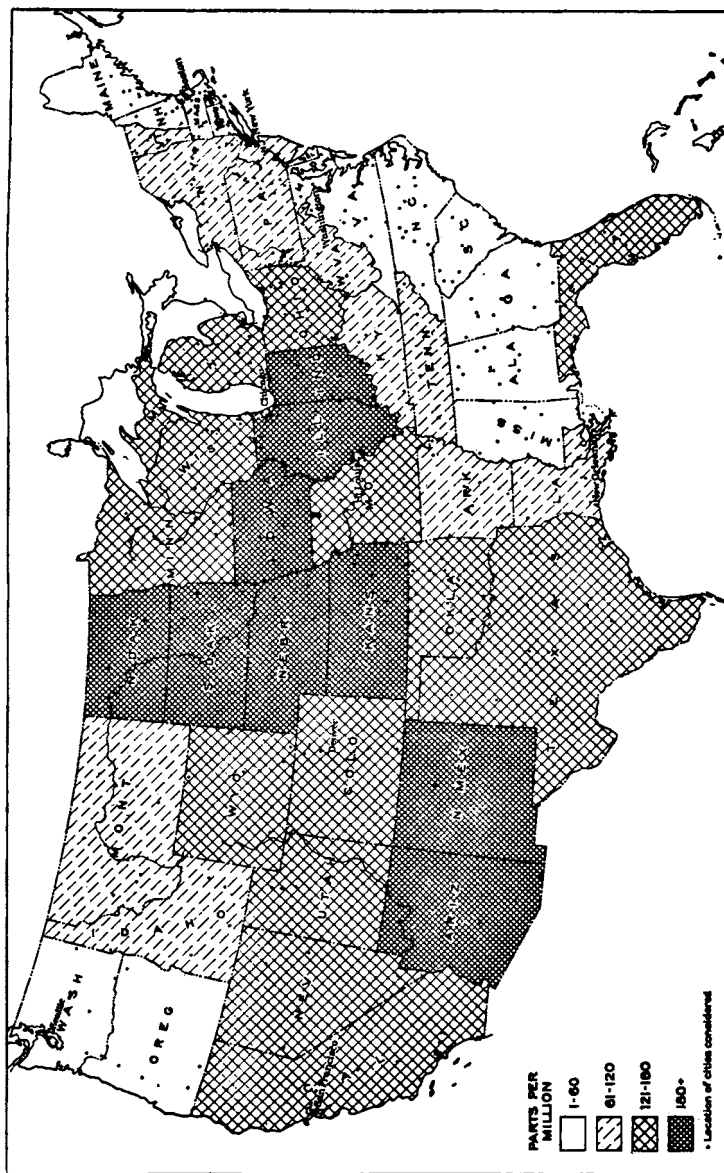
Fig. 52—Weighted average hardness, by states, of water furnished in 1932 by public supply systems in over 600 cities in the United States. (*Courtesy U. S. Geological Survey.*)

produce a lasting foam on shaking. The amount of soap destroyed is usually converted to its equivalent of calcium carbonate, whether the actual reaction was with carbonate, sulfate, chloride or nitrate of calcium or magnesium. Hardness is therefore frequently reported as the amount in parts per million of calcium carbonate equivalent to all the calcium, magnesium and other constituents that contribute to hardness.

Degree of hardness should be distinguished from another determination usually made on water, namely its total solids content. This is obtained by evaporating a measured amount of water and weighing the solid residue. To determine the percentage of mineral constituents present in total solids, the residue may then be further heated at high temperatures. The loss in weight is usually referred to as loss on ignition, which constitutes organic matter, carbon dioxide and others.

The hardness caused by the calcium and magnesium equivalent to the bicarbonate in a water is called "carbonate hardness" and the remainder "noncarbonate hardness." These terms approximate, respectively, the older designations "temporary hardness" and "permanent hardness." Temporary hardness is so called because the bicarbonate of calcium decomposes upon heating to form the corresponding insoluble carbonates which then precipitate out. All other salts of calcium and magnesium are largely unaffected in their solubility by heating and therefore remain in solution, constituting the permanent hardness.

On the basis of hardness, natural water may be classified rather arbitrarily somewhat as follows (*307*):

Hardness	Classification
0 to 15 p.p.m.	Very soft water
15 to 50 p.p.m.	Soft water
50 to 100 p.p.m.	Medium hard water
100 to 200 p.p.m.	Hard water
Greater than 200 p.p.m.	Very hard water

The following brief review of the individual substances normally occurring in natural waters is designed merely to outline some of the problems which each may present at times.

From what has been said above about the role of calcium and magnesium ions as the two principal water hardening agents, it is evident that the objectionable features of hard waters are closely associated with the calcium and magnesium salts. Thus the scale which forms in water systems and which greatly reduces the operating efficiency of such equipment as boilers, water heaters, heat exchangers, hot water lines, etc., consists in general of calcium and magnesium carbonate or sulfate with smaller or larger quantities of silica and iron. Since heat renders the carbonate salts

of calcium and magnesium largely insoluble, these precipitate out to form a sludge in water systems which may prove troublesome. Thus cases are known where the steam used in baking ovens carried over such precipitated hardness curds to produce unsightly spots on the top crust of loaves. This can usually be guarded against by installing proper steam traps in the steam lines or by proper treatment of the water. Excessive amounts of calcium and magnesium, in the form of their bicarbonates, are also responsible for the high alkalinity found in some natural waters, although some sodium bicarbonate may also occasionally be present. The bicarbonates are formed by the reaction of carbon dioxide present in rain and surface waters with dissolved limestone. Excess alkalinity is undesirable, especially if derived from bicarbonates, since these salts possess a considerable buffer effect and hence resist the action of acids to lower the pH. Thus doughs made with alkaline waters show abnormal fermentation because the pH level remains above the optimum range for yeast and enzymatic activity. Water alkalinity may also be due partly to so-called hydrate alkalinity derived from the presence of hydroxyl ions. These are not encountered in natural waters except when high contamination by alkaline trade wastes occurs.

The sulfate ion is present in all natural waters. The quantity of sulfates found in natural waters varies considerably with variations in the mineral content of the soil in different localities. In process water the principal objection to the sulfate ion is that it combines with calcium to form calcium sulfate scale which is most frequently encountered in boilers which use untreated water. On the other hand, the presence of calcium sulfate is desirable in dough waters for its stimulating effect upon yeast and its tightening effect upon dough consistency. For these reasons, calcium sulfate is a normal constituent of yeast foods or dough conditioners.

Chlorides of calcium, magnesium, sodium, potassium and other cations are normally found in all natural waters. Chlorides are highly soluble and therefore are not usually involved in scale formation to a marked degree. In general, natural waters do not contain sufficient amounts of chlorides to exert a noticeable effect upon dough behavior. The addition of common salt (sodium chloride) to dough is far in excess of any concentrations found in natural waters. High chloride values in natural waters may indicate the presence of animal pollution and therefore suggest the need of bacteriological and sanitary analyses of such high chloride waters.

Since silicon is one of the most abundant elements found in the earth, it is quite natural that it should occur in varying amounts in different waters. Silica may occur both in a soluble form and in a colloidal form.

Colloidal silica is present as a suspension which can be removed by proper coagulation and filtration. Soluble silicates, on the other hand, are more difficult to eliminate and, if present in excessive amounts, cause difficulties by forming an extremely hard scale. The silica content is usually greater in waters of low hardness and high alkalinity. Silicates are rather inert salts and have been found to exert no perceptible influence upon fermentation and general dough characteristics.

Phosphates and sulfites do not as a rule occur in natural waters, except where contamination by trade wastes takes place. Interest in them is therefore limited. Iron is found frequently in natural waters and is objectionable chiefly because it will form stains that discolor equipment with which it comes into contact. The same holds true to a considerable extent of manganese which usually occurs in waters containing iron. It may cause difficulties at times by depositing in the form of black manganese hydroxide, thereby clogging pipes and valves, and also discoloring processing equipment.

Nitrates occur in natural waters in relatively small quantities. They are derived as a rule from nitrogenous substances which are subsequently oxidized to nitrates. High nitrate contents may be indicative of contamination of the water supply with sewage.

In addition to mineral constituents, raw and treated waters also usually contain dissolved gases, including chlorine, oxygen, carbon dioxide, hydrogen sulfide, and nitrogen. Chlorine is not found in natural waters but is added as a bactericidal agent in water treatment plants to render the water supply safe for human consumption. The amount of chlorine added for this purpose will vary with the degree of bacterial contamination encountered, but as a rule the aim is to chlorinate water sufficiently to maintain a chlorine residue of at least 0.2 p.p.m. At these concentrations, chlorine has no effect upon the taste of the water nor does it influence the course of yeast fermentation. Chlorine should not be confused with chloride which is a negative ion, whereas chlorine is a gas dissolved in water.

Dissolved oxygen in water is derived from atmospheric oxygen. As a general rule, surface waters contain a greater amount of this gas than do ground waters. Soft waters tend to show higher dissolved oxygen contents also, since the presence of mineral substances in water reduces the solubility of oxygen. The presence of dissolved oxygen in water is objectionable principally because of the corrosiveness which this gas imparts to water.

Free carbon dioxide, which should be distinguished from the combined carbon dioxide present in the form of bicarbonate and carbonate ions, also occurs in various concentrations in water. It is principally derived

from decaying organic matter rather than from the atmosphere whose normal carbon dioxide content is too low to be of influence. As a rule ground waters carry more dissolved carbon dioxide than do surface waters. As in the case of oxygen, the principal objection to dissolved carbon dioxide is the corrosiveness it imparts to waters. Carbon dioxide in solution ionizes to form unstable carbonic acid, reducing thereby the pH of the water and increasing its corrosive character. Severe corrosion of pipes, water jackets, valves and heat exchangers may take place when water of high carbon dioxide content is employed.

Hydrogen sulfide is a gas with a pronounced rotten-egg odor. This odor is imparted to water even when only minute traces of the gas are dissolved. In addition to the odor problem, this gas also renders the water highly corrosive.

In addition to dissolved minerals and gases, waters frequently are also contaminated by suspended impurities, such as mud, silt or clay, and by organic impurities represented by microbial animal and plant life. These impurities are most frequently encountered with surface waters.

WATER TREATMENT

It is only on relatively rare occasions that natural waters as encountered are suitable in all respects for the specific requirements of different industries and for different applications. Thus in a bakery, water suitable for ingredient purposes may require treatment before it can be safely used for heating, cooling, washing, and other purposes. Recent years have seen marked progress in water correction methods so that it is today possible to process natural waters efficiently and economically to meet nearly every industrial requirement. The principal purpose of water conditioning is to provide water which is neither scale forming nor corrosive so that it will not attack equipment and cause costly repairs. Whether or not an individual plant should resort to water treatment depends upon local conditions. It may generally be taken for granted in the case of water obtained from municipal supplies that it is safe for human consumption from a bacterial viewpoint, free from offensive odors and tastes, and adequately filtered for removal of turbidities caused by suspended matter. In recent years an increasing number of municipalities have also adopted some means for the reduction of excessive hardness. Hence, many bakeries obtaining their water from public supplies do not have to subject it to further treatment. This is generally the case with retail bakeries and with larger plants located in big cities. The situation may not be quite as favorable in plants operating in smaller communities or in plants which have to depend to a greater or lesser extent upon private water supplies.

Clarification processes are required where the available water shows turbidity due to the suspension of finely divided solids. These may be partially removed by sedimentation in special basins or tanks, provided the impurities have a sufficiently high settling rate. Otherwise it is necessary to treat the water with a coagulant. The most widely used reagent for this purpose is aluminum sulfate. This material is fed to the

Fig. 53—Water treatment station consisting of sand and activated carbon filters. (*Courtesy Helms Bakery*.)

water in properly adjusted dosages by means of a chemical feeder. It reacts with the natural alkalinity of the water or with added alkalinity to produce a gelatinous precipitate which engulfs the impurities and forms a floc which is then removed by settling and filtration. The application of the sedimentation and flocculation processes requires rather large areas for the necessary basins and is therefore not ordinarily suitable in connection with bakery water treatment.

The second method of water clarification is by filtration. Although many types of water filters are available, the most suitable for bakery use is the so-called pressure-type vertical sand filter. This filter consists of a cast iron or steel shell which permits filtration to take place under a given pressure (see Figure 54). The filter bed consists of several graded

layers, with coarse gravel at the bottom, then several layers of finer gravel, followed by a layer of coarse sand and finally a layer of fine sand on the top. The filter medium is usually sand, but may consist of other substances, such as crushed and graded anthracite, charcoal, carbon, marble, etc. The filter bed is supported by a deflector plate which separates the bed from the underdrain system at the bottom in which the filtered water collects and from whence it is piped to service. In the operation of the filter, the raw water enters at the top, which is provided with some sys-
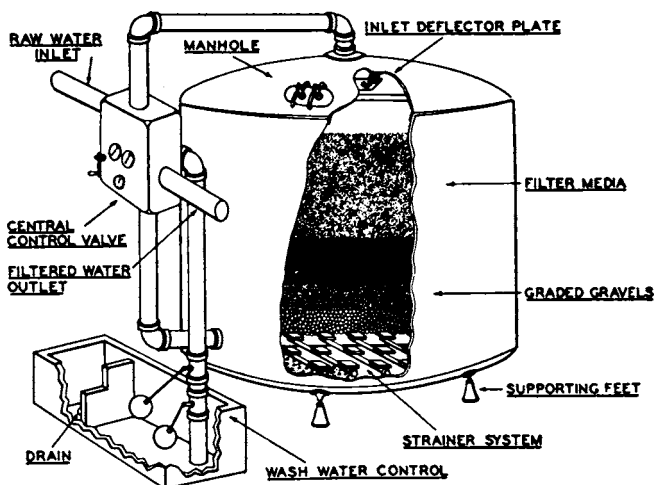
Fɪɢ. 54—Vertical pressure filter. (*Courtesy Hungerford & Terry, Inc.*)

tem for evenly distributing the water over the entire filter area, passes slowly through the fine sand layer and the successive coarser supporting layers and finally collects in the space between the bottom of the filter and the false bottom. The removal of suspended impurities takes place at the surface of the filter bed. Eventually the accumulation of suspended matter will clog up the fine sand pores, thereby greatly reducing the flow of water through the filter, and it then becomes necessary to cleanse the filter. This is accomplished by backwashing, in which the flow of water is reversed. By passing water at relatively high velocity upward through the filter and out to the drain, the filter bed is expanded, the sand particles cleansed, and the accumulated scum washed out of the filter. A further beneficial effect obtained is the regrading of the filter bed. During filtration the fine sand particles tend to migrate downward and these are then again carried upward by the force of the backwashing water. Backwashing usually requires about ten minutes. The frequency with which it must be carried out depends upon the amount of impurities present in the raw water.

While clarifying processes remove suspended solids from the water, they have no effect upon dissolved solids, whether organic or inorganic in nature. Where objectionable tastes and odors in water are due to dissolved or colloidal organic compounds, sand filtration will also prove ineffective in their removal. In such cases, sand filtration must be supplemented by activated carbon filters which remove such impurities by a process of adsorption.

After water has been freed from impurities, tastes and odors, it is frequently suitable for most bakery uses. In cases where the water is excessively hard, it must be subjected to further softening treatment. There are four general types of water softening processes: (1) distillation, (2) base-exchange processes, (3) demineralizing processes, and (4) lime-soda processes. Distillation is too costly to be of practical value so that the selection is reduced to the three latter categories.

Base-exchange, or cation exchange, processes include the sodium zeolite and hydrogen zeolite softening methods. Zeolites are finely granulated solid substances which possess the property of replacing certain cations, or positively charged ions, with other ions of equivalent positive charge. Natural zeolites consist principally of sodium aluminum-silicate, while synthetic zeolites, developed within the past several years, are of a carbonaceous nature. In sodium zeolite softening, the zeolite reacts with all cations present in the water with a positive charge of two or more, and replaces them with sodium ions. Since the two principal cations of hard water are calcium and magnesium, their removal is the primary function of sodium zeolite. The basic chemistry involved in this reaction, using calcium as the example, may be represented as follows:

$$Ca^{++} \quad + \quad Na_2Z \quad = \quad CaZ \quad + \quad 2Na^+$$

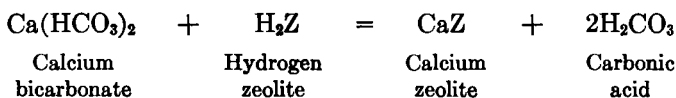| Calcium | Sodium Zeolite | Calcium Zeolite | Sodium Ions |
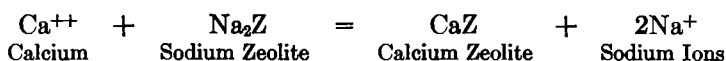
The calcium ions, responsible for water hardness, are thus removed by interaction with the zeolite and are replaced by sodium ions of corresponding positive charge. It should be noted that the total solids content of the water is not reduced but that the nature of the salts is merely changed from calcium (and magnesium) carbonates to sodium carbonate. Since the latter is highly soluble it does not form scale or sludge in water systems nor does it form insoluble scum with soap. The water has hence been rendered soft. It is evident from the above equation that eventually most of the sodium of the zeolite will be replaced by calcium and magnesium so that ultimately the zeolite will cease to function. When this point is reached, the zeolite must be regenerated. This regeneration is accomplished by washing the zeolite bed with a strong solution of sodium chloride in which the high concentration of sodium ions reverses the

above reaction, replacing the calcium ions in the exhausted zeolite, the liberated calcium ions then combining with the chloride ions to form calcium chloride which is run to waste.

Zeolite filters resemble pressure sand filters in general appearance and construction. They generally consist of a steel shell. The bottom layer of the filter bed is made up of graded gravel on which is placed the zeolite to a depth of 30 or more inches. Water enters at the top, passes through the zeolite and collects in an underdrain. The size of the zeolite bed will depend upon the type of zeolite, the hardness of the water, and the volume to be treated between regenerations. Regeneration is carried out by first backwashing the filter to remove impurities from the filter bed, then a strong salt solution is added at the top, followed by a clear rinse water to remove both the calcium and magnesium chloride formed and the excess salt solution.

In *hydrogen zeolite softening,* in which zeolites of non-siliceous organic nature are employed, the cations are replaced by hydrogen instead of sodium, thereby changing the various salts into their corresponding acids. Thus if a water is treated in which the predominant hardening salts are the bicarbonates of calcium and magnesium, the softened water will be largely freed of its solids, the cations being taken up by the zeolite while the bicarbonate radicals are changed into carbonic acid, according to the following chemical equation:

$$Ca(HCO_3)_2 \quad + \quad H_2Z \quad = \quad CaZ \quad + \quad 2H_2CO_3$$

| Calcium bicarbonate | Hydrogen zeolite | Calcium zeolite | Carbonic acid |

Carbonic acid is a rather unstable compound which breaks up into water and carbon dioxide on aeration, with the carbon dioxide being removed in the process. In waters containing sulfates and chlorides, these are changed into sulfuric acid and hydrochloric acid which may require neutralization by the addition of alkali. The hydrogen zeolite will also remove sodium, iron and manganese ions. When the zeolite is exhausted it is regenerated by backwashing and treatment with acid, sulfuric acid being most generally used for this purpose.

The demineralization process is actually a continuation of hydrogen zeolite softening (see Figure 55). This process, as has been seen, removes the cations, such as calcium, magnesium, sodium, etc., but leaves the anions, or acid radicals, unaffected. These remain in the water to form mineral acids. Recent developments in water research now make possible the removal of these acid radicals also, producing water which approaches distilled water in purity. The materials employed for this purpose are certain resins and the process is called "Anion Exchange." Actually there

is no ionic exchange but a direct adsorption of the acids by the exchange material (*307*). Hence if water treated by hydrogen zeolite is passed through an anion exchanger its purity will be close to that of distilled water. Waters of such high purity are employed for specialized purposes only and find no application in the bakery. However, the demineralization process may be employed to solve unusual water problems. In many instances of high permanent water hardness, part of the water can be
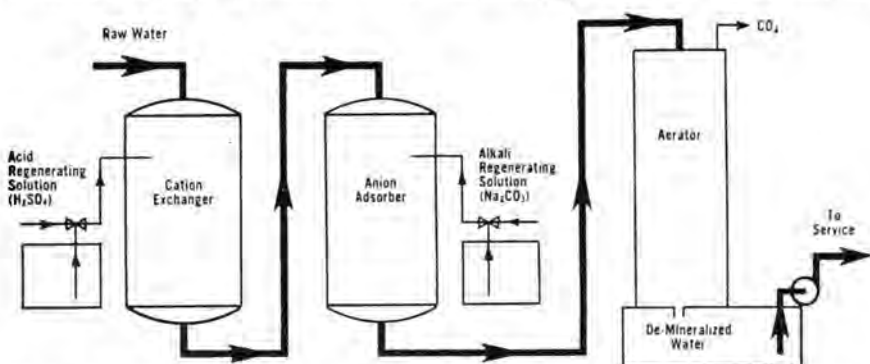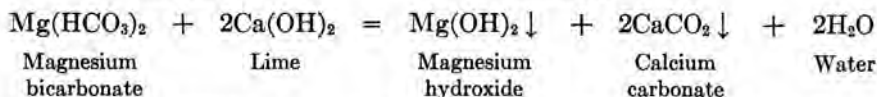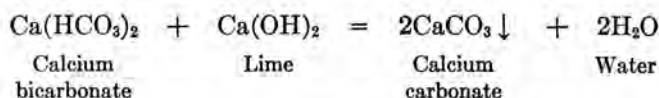

FIG. 55—Diagram of cation-anion exchanger demineralization unit. (*Courtesy W. H. & L. D. Betz.*)

demineralized for blending with raw water to yield a supply of medium hard water suitable for the purpose at hand.

Lime-soda softening of water is obtained by the use of lime (calcium hydroxide) and soda (sodium carbonate) which remove the calcium and magnesium salts causing the hardness in water. Depending upon whether the process is carried out at normal raw water temperatures or at boiling temperatures, it is called either the "cold process" or the "hot process."
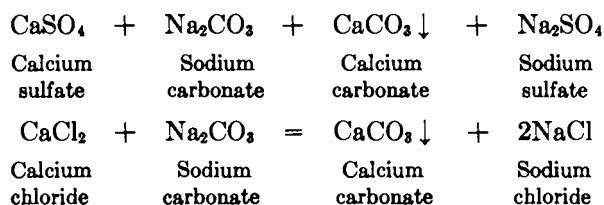
The effectiveness of the process is best indicated by presenting some of the basic chemical reactions which take place during the treatment. The calcium and magnesium bicarbonates representing the chief water hardening constituents react with the lime to form insoluble compounds which then precipitate out, according to the following equations:

$$Ca(HCO_3)_2 \ + \ Ca(OH)_2 \ = \ 2CaCO_3 \downarrow \ + \ 2H_2O$$

| Calcium bicarbonate | Lime | Calcium carbonate | Water |

$$Mg(HCO_3)_2 \ + \ 2Ca(OH)_2 \ = \ Mg(OH)_2 \downarrow \ + \ 2CaCO_2 \downarrow \ + \ 2H_2O$$

| Magnesium bicarbonate | Lime | Magnesium hydroxide | Calcium carbonate | Water |

The precipitated calcium carbonate, magnesium carbonate and magnesium hydroxide are removed by settling and filtration. Hence there is

a marked reduction in the total solids content of the water brought about by treatment with lime, at least in the case of waters high in carbonate hardness. In many cases treatment with lime alone will prove sufficient to render a water suitable for a given purpose.

However, lime reacts with magnesium salts constituting the non-carbonate hardness to produce soluble calcium salts, thereby maintaining its permanent hardness. Furthermore, the raw water itself may contain soluble calcium salts, such as calcium sulfate, calcium chloride, etc. These must also be removed if adequate softening is to be effected and this is accomplished by the use of soda ash, or sodium carbonate, as is shown by the following equations:

$$CaSO_4 \quad + \quad Na_2CO_3 \quad + \quad CaCO_3 \downarrow \quad + \quad Na_2SO_4$$

| Calcium sulfate | Sodium carbonate | Calcium carbonate | Sodium sulfate |

$$CaCl_2 \quad + \quad Na_2CO_3 \quad = \quad CaCO_3 \downarrow \quad + \quad 2NaCl$$

| Calcium chloride | Sodium carbonate | Calcium carbonate | Sodium chloride |

It will be seen that the soluble calcium salts are changed into insoluble carbonates which precipitate out. In contrast with the reactions with lime, however, there is little actual reduction in the solids content because of the formation of soluble sodium salts. Nevertheless, practically all of the water hardening salts are removed and a decided softening effect is obtained.

The lime-soda process may be carried out by means of various systems, such as the intermittent or batch system, or the continuous system, both of which are employed with various modifications. Detailed descriptions may be found in the Handbook prepared by W. H. & L. D. Betz (*307*).

In addition to the mineral constituents and other impurities of water, attention must also be given to its biological purity, especially where the water is obtained from private wells or surface supplies. While as a rule the bacterial contamination of ground water is less marked than that of surface water, most ground waters harbor some microbial flora which may render their use as ingredient water unsafe without previous sterilization. The presence of even occasional contamination by pathogenic bacteria demands the adoption of continuous sterilization. The most widely used process for insuring the biological purity of water is chlorination in which chlorine gas or highly unstable chlorine compounds are added to the raw water either prior to or after filtration. The sterilizing agent is fed to the water by means of special chlorinators of different designs. The extent to which chlorination is to be carried out depends, of course, upon the degree of contamination of the water by bacteria, organic

matter and inorganic impurities. The actual dosage should be determined by a reliable bacteriological laboratory on the basis of comprehensive water analyses.

Water treatment constitutes a specialized science. Hence it is advisable for bakers confronted with water problems to engage the services of competent and reliable engineers and chemists who specialize in the conditioning of water for industrial purposes. It is also good practice to obtain periodically complete water analyses, especially where the supply consists of surface waters, to detect seasonal variations in the character of the water which may have an adverse effect upon the uniformity of the baked products. This is of special importance in the case of municipalities which draw for their supplies upon different sources, such as surface, shallow and/or deep well sources, changing from one to the other as varying requirements may demand. It is not unusual for the hardness of municipal waters, for example, to vary tenfold from their low to their high levels within a matter of a few weeks or months. That such drastic changes are bound to exert an effect upon bakery operation is quite obvious.

EFFECTS OF VARYING DOUGH WATERS

Water represents a large proportion of the dough so that even relatively small percentages of active ingredients dissolved in it exert a pronounced effect upon dough character and bread quality. A water containing a medium degree of hardness is considered most suitable for baking purposes since some of the mineral salts have a strengthening effect upon the gluten of the dough and serve to some extent as yeast foods. Excessively hard waters are undesirable because of their retarding influence upon fermentation. Soft waters are objectionable because they tend to soften the gluten and yield a soft sticky dough. One of the original functions of yeast foods was to correct the mineral deficiency of these waters by supplying salts that serve to strengthen the gluten on the one hand and provide necessary mineral nutrients to the yeast. Alkaline waters are undesirable because of their deleterious effects upon fermentation. Such waters contain excessive contents of alkaline salts which tend to neutralize the normal acidity developed during yeast fermentation. Since the functions of both flour enzymes and yeast enzymes are significantly affected by the pH of the medium, with the enzymes acting at their optimum at pH levels between approximately 4 and 5, it is evident that excessively alkaline waters which raise the pH of the dough above the optimum range for enzyme activity have a pronounced effect upon the course and character of fermentation.

In evaluating the suitability of a particular type of water for baking,

it should be kept in mind that not all of the minerals present in the water exert an effect upon fermentation. Thus Mary Brooks (*308*) points out that the following salts, in the quantities and form normally encountered in natural waters, are without effect: copper salts, iron salts, aluminum salts, tannic acid, silicates, and phosphates. Except for copper salts and tannic acid, all the other above minerals are ordinarily found in natural waters.

Salts which have been found to produce an effect upon fermentation, either favorable or unfavorable, are the following, according to the same author: calcium oxide, calcium carbonate, calcium sulfate, magnesium chloride, magnesium oxide, and sodium bicarbonate. As has been seen, the quantitative presence of these salts principally determines the character of a particular water, i.e., whether it is alkaline, hard, or saline. Brown (*309*) studied systematically the effects of seven different salts upon yeast fermentation and bread character. He used concentrations ranging from 50 p.p.m. to 1000 p.p.m. and employed both the sponge dough and the straight dough methods. The controls were carried out with distilled water. He found that sodium bicarbonate in concentrations of 100, 500 and 1000 p.p.m. did not appreciably influence the fermentation. Magnesium oxide, in concentrations of 50, 250 and 500 p.p.m. also showed little effect, nearly identical loaf volumes being obtained with the sponge method at all concentrations used, while the straight dough method produced somewhat smaller volumes. Magnesium chloride, used at the same concentrations as magnesium oxide, had a marked beneficial effect upon fermentation, yielding stiffer doughs and producing larger volumes than the control with distilled water. Best dough volume was obtained with 50 p.p.m. of magnesium chloride. Beneficial results were also obtained with calcium carbonate at all concentrations used, namely 100, 500 and 1000 p.p.m. Largest loaf volume was given by water containing 500 p.p.m., and stiffer doughs were obtained at all concentrations. Calcium sulfate in concentrations of 50, 250 and 300 p.p.m. also had a beneficial effect on fermentation, resulting in larger loaf volume and stiffer doughs. Calcium hydroxide, in concentrations of 100, 500 and 1000 p.p.m., had a marked deleterious effect on fermentation at the higher concentrations, the influence being less pronounced at 100 p.p.m. The alkalinity of the calcium hydroxide waters at the higher concentrations was sufficient to destroy the activity of yeast when the yeast was suspended in the water prior to its addition to the dough. The adverse effects of alkaline waters can be partly overcome by adding the yeast directly to the flour rather than first suspending it in the alkaline water, the improvement resulting from the neutralization of the water's alkalinity by the natural acidity of the flour so that yeast activity is not impaired by

exposure to the full alkalinity of the water. In evaluating the results obtained by Brown with the different salts studied it should be kept in mind that the test doughs and loaves were compared with controls made with distilled water. The controls therefore did not represent optimum standards so that the improving effects observed would be less pronounced had a more suitable baking water been used for the controls.

Loving (*310*) has shown that not all yeasts react identically to the different mineral constituents of water. Thus some yeasts show an exceptional tolerance toward high alkalinity, being able to produce normal fermentations with alkaline waters which would inactivate other yeasts. Hence, where alkaline waters are prevalent and where water conditioning is not practiced, the proper choice of yeast becomes a matter of considerable importance. The suitability of a yeast is best determined by obtaining yeast samples from different sources and making up small experimental doughs under identical conditions, using a different yeast for each dough and comparing the fermentation results.

Juvrud (*311*) investigated the effects of two conventional types of yeast food when used with waters of varying mineral composition. The waters tested were made up in the same manner as those by Brown (*309*), i.e., single salts were used in concentrations ranging from a low of 50 p.p.m. to a high of 1000 p.p.m. in the case of some of the salts. His findings were in agreement with the practical observation that yeast foods tend to minimize the adverse effects of excessively hard waters on fermentation and on general bread quality.

Pickering (*312*), reviewing the practical implications of soft, hard, and alkaline waters for baking, summarizes their respective effects as follows: Soft waters will generally yield a soft and sticky dough because the gluten tightening effect of minerals is absent. As a result the absorption may have to be reduced by as much as 2 percent to obtain workable doughs. Although gas production in soft water dough is normal, gas retention is adversely affected and the dough has the appearance of being young although this may not be the actual case. The somewhat lower pH that is characteristic of soft waters has an accelerating effect on fermentation, requiring some reduction in fermentation time. While soft water may yield bread of fairly good loaf volume and very even grain, texture and color are apt to be poor. Corrective steps include an increase in the use of yeast food and of dough salt.

Hard waters retard fermentation by toughening the gluten too much. Increasing the amount of yeast will assist in correcting this condition by a more vigorous fermentation and softening of the gluten. The use of diastatic malt and a decrease in the amount of yeast food are also recommended. In baking tests with various hard waters the doughs tight-

ened up well, carried normal absorption, and gave good oven spring, grain and texture.

Alkaline waters have a tendency to reduce the rate of fermentation and therefore require an increase in fermentation time, unless small additions of acidifying agents, such as vinegar, are added to the dough. A slight increase in yeast food to correct the deficiency in calcium sulfate which characterizes such waters will generally aid in accelerating gas production. Normal absorptions may be used with alkaline waters which, when used in doughs, produce good crumb color, grain and texture, though a smaller loaf volume, unless fermentation time and the mineral salts content are properly balanced.

Skovholt (*313*) has expressed the opinion that the normal variations encountered in the reported mineral contents of different natural waters are not sufficient to account for the variability in dough characteristics which are attributable to differences in water. Thus he points out that in only 9 of the 48 States is there a hardness of more than 180 p.p.m. when averaging the waters analyzed. This figure is equivalent to about 120 parts of mineral per million parts of flour when such water is used in baking. An average yeast food level will contribute about 1000 parts of calcium sulfate per million parts of flour, and sodium chloride, used in normal amounts, will be present in amounts of about 20,000 p.p.m. of flour. In view of such levels, it is difficult to understand why waters differing by 100 or 200 p.p.m. in hardness (expressed as calcium sulfate) should markedly alter dough characteristics. The answer appears to lie in the presence of certain trace elements which are not reported in water analyses. As an example, vanadium present in only a fractional part per million has a decisive effect on dough characteristics. Most natural waters contain such trace elements and it is the difference in the nature of these elements that appears to account for the different effects produced by natural waters. This view finds support in the fact that artificially prepared waters, such as used in the studies of Brown (*309*), differing widely in content of the components ordinarily listed in water composition tables, have shown little or no difference in effects upon dough characteristics.

COMMON SALT

In its chemical meaning the term salt refers to any compound produced by the interaction of a base and an acid in which the hydrogen of the acid is substituted by a metal or a group of elements acting as a metal. Common salt, or, simply salt, refers to sodium chloride which is a white crystalline product, consisting of the elements sodium and chlorine, and has the chemical formula NaCl.

Salt occurs in the sea, in salt lakes, natural brines, and as underground deposits in the form of rock salt. It is obtained from the sea and natural brines by means of evaporation of the aqueous solution either with the aid of solar heat or by artificial heating. As evaporation proceeds, the various salts present in the solution crystallize out in the reverse order of their solubility, the least soluble separating out first and the most soluble last. This fractional separation permits a far-reaching purification of the salt. Underground deposits may be processed in two different ways. Rock salt may be mined, the salt being brought to the surface in fairly large lumps
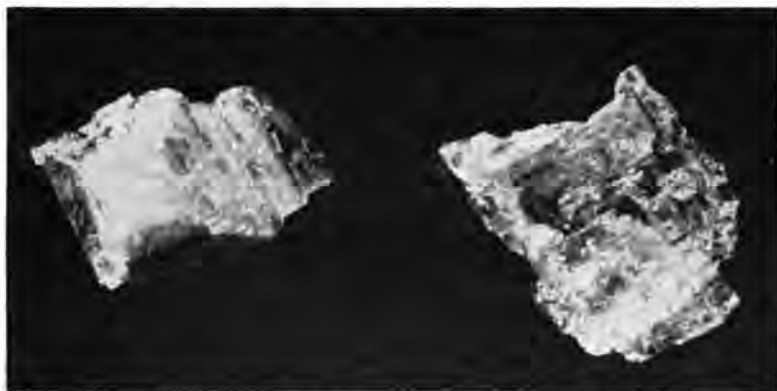
FIG. 56—Coarse salt particles produced by the Grainer system of refining (magnified). (*Courtesy Diamond Crystal Salt Co., Inc.*)

which are then crushed, ground and graded according to size. This process is possible with deposits of high purity. Where less pure deposits are encountered, the usual procedure is to drill wells into the deposit, pumping water under pressure into them. The water, when saturated with the salt, is then forced to the surface through a brine pipe by the pumping pressure applied to the fresh water. The brine will carry only the soluble components of the salt deposit, leaving behind all insoluble impurities. On reaching the surface the brine is stored in huge storage tanks prior to its refining.

Salt refining methods consist essentially of evaporating the brine, gathering the resultant salt crystals, washing and drying them, and grading them according to size and purity. Depending upon the specific refining method used, salts of different rates of solubility and of different degrees of purity are obtained. In the so-called Grainer system, which is the oldest and most widely used, the brine is run into large open tanks equipped with heating pipes which heat the solution and cause the water to evaporate. As concentration increases coarse crystals of salt begin to form on the surface and sink to the bottom of the pan. Automatic

rakes gather the salt into a trough at one end where a swift-flowing brine carries it to the washer and dryer. Salt obtained by this process consists of relatively large and coarse crystal structures, shown in Figure 56, with a slow rate of solubility.

A modification of the above process consists of the use of closed pans to which a vacuum can be applied. This vacuum process is more economical since lower evaporative temperatures are employed. The brine is run through a series of large vacuum pans, each of which has a progressively higher vacuum applied to it. The resultant salt is obtained in a granular, cube-shaped form of considerable hardness and medium
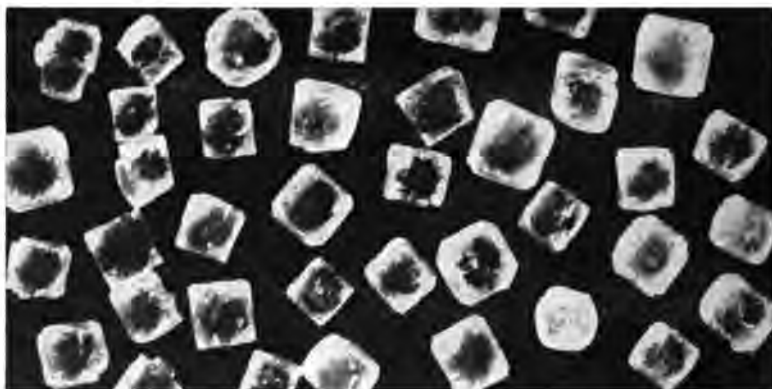
FIG. 57—Granulated salt cubes produced by the vacuum system of refining (magnified). (*Courtesy Diamond Crystal Salt Co., Inc.*)

rapid solubility. The cube-shaped structure of granulated salt is shown in Figure 57. A familiar example of this type of salt is the common table salt.

A third process, the so-called Alberger process, is employed to obtain flake-like salt of exceptional purity and rapid solubility. In this process the brine is heated in several steps to 290° F., being kept under pressure to prevent boiling. The hot brine is then passed through a graveler which is a tank filled with cobblestones on which the high temperature-insoluble impurities are deposited. The purified brine then has its pressure reduced in a series of so-called flashers which also produce a decrease in the brine's temperature and cause initial crystallization of the salt. The brine enters an evaporator pan in which crystallization is promoted, the depositing crystals being raked automatically into a so-called salt well from whence they are conveyed into a centrifugal separator in which most of the brine adhering to the flake-like crystals is removed. The semi-dried salt next passes through a rotary dryer for complete drying and is then graded by means of screens into different particle sizes. A magnified

view of the delicate flake-like crystals obtained by this process is shown in Figure 58.

Salt of highest purity only should be used for baking purposes. Modern refining methods now make possible the production of baker's salt that approaches absolute purity and that has an extremely rapid rate of solubility. Such salts have a pure salt taste without the objectionable bitter after-taste that characterizes less pure products.

Salt performs a three-fold function in bread doughs. It has a stabilizing influence on fermentation, enabling the baker to control the development of yeast, the production of gas and other by-products of fermenta-

FIG. 58—Flake-like salt crystals produced by the Alberger system of refining (magnified). (*Courtesy Diamond Crystal Salt Co., Inc.*)

tion, and the ripening of the dough. Secondly, salt has a strengthening and tightening effect on the gluten of dough, which may be due in part to its inhibiting action on proteolytic enzymes as shown by Miller and Johnson (*314*). This influence becomes particularly important in instances where very soft water is employed for dough mixing or where inadequately matured flours must be used. Under both conditions difficulty is likely to be encountered with soft and sticky doughs. The use of maximum amounts of salt will help correct these difficulties. The third and most important function of salt is the improvement of flavor. Bread from which salt has been omitted is unsaleable because of its flat, insipid taste.

The amount of salt to be added to the dough should be calculated on the basis of total dough weight rather than on the flour weight basis. Dunn (*315*) has shown that the use of flour weight as the reference for salt addition may lead to reduced salt contents of doughs. Thus he cites examples of formulas, all based on 100 lbs. of flour and calling for 2 lbs. of salt, which, because of the varying amounts of enriching ingredients used, result in dough weights ranging from 166 lbs. to 203.5 lbs. and actual

salt contents of 1.20 percent to 0.98 percent. If 1.2 percent is taken as the optimum salt content, then obviously doughs with lower contents were deficient in salt even though the same percent based on flour weight was used in all instances. Dunn has recommended the following average increments of salt for various products: sweet doughs, 5 ounces per gallon of mix; Danish pastry, 6 ozs. per gallon; cake batter, 0.5 oz. per pound of flour; cookie doughs, 0.5 to 1 oz. per 10 lbs. of dough; rich icing, 0.5 oz. per 10 lbs. of sugar; lean icing, 0.25 oz. per 10 lbs. of sugar; pie dough, 0.5 oz. per pound of flour.

YEAST FOODS

In addition to common salt, bakers use other salts of various reactivity and for different purposes. These are usually referred to as yeast foods, dough conditioners, dough maturing agents, etc., the terminology used being frequently loose and often inappropriate. Technically speaking, yeast foods are all substances, such as fermentable carbohydrates, amino acids, and minerals necessary to support the growth and activities of yeast. In the average type of so-called yeast food, usually only one salt serves this particular function, and that is the ammonium salt which, on dissociation, yields ammonium ion which is utilized by the yeast as a source of necessary nitrogen. The other salts present in a yeast food act in an entirely different capacity, serving either as oxidizing agents or as water correctives, or both. On the other hand, the term dough conditioner implies an action directly upon the colloidal character of the dough, either through modification of its gluten, its state of oxidation, or the surface tension between its aqueous and fat phases. Yet many dough conditioners also contain ammonium salts for the specific purpose of accelerating yeast action. In this brief discussion all the various products will be referred to simply as dough conditioners.

The most commonly used oxidizing salts in doughs are potassium bromate ($KBrO_3$), potassium iodate (KIO_3), calcium peroxide (CaO_2), ammonium persulfate (($NH_4)_2S_2O_8$) and potassium persulfate ($K_2S_2O_8$). While their over-all effect is essentially the same, bringing about an improvement in dough characteristics that lead to larger bread volumes, improved grain and texture and better loaf symmetry, their function is not identical and the selection of the appropriate oxidizing agent for different types of flour, different plant conditions, varying water supplies, etc., must depend upon practical experimentation at the shop level. Based upon observations of practical results obtained with these various salts, certain generalizations may be made. Compared with potassium bromate as the oldest and most widely used oxidizing agent, potassium iodate acts at somewhat higher pH levels and gives a slightly drier dough with im-

proved machinability. Its effect is felt earlier in the fermentation, giving rise to bold, lively sponges, and it imparts a greater fermentation tolerance to dough. Because of its more pronounced effect, it must be used in smaller increments than the bromate. Calcium peroxide has an action which is less marked than that of bromate and which probably differs in kind also. It has a strengthening effect upon gluten and yields somewhat drier doughs. This permits an increase in absorption and a reduction in the amount of dusting flour during the make-up stage. Ammonium and

TABLE 102. COMPOSITION OF REPRESENTATIVE
TYPES OF DOUGH CONDITIONERS

Type I

Calcium acid phosphate	50%
Sodium chloride	19.35
Ammonium sulfate	7.0
Potassium bromate	0.12
Potassium iodate	0.10
Starch (as filler)	23.43

Type II

Calcium sulfate	25.0%
Ammonium chloride	9.7
Potassium bromate	0.3
Sodium chloride	25.0
Starch	40.0

Type III

Calcium peroxide	0.65%
Ammonium phosphate⎫ Di-calcium phosphate⎭	9.0
Starch or flour	90.35

potassium persulfates tend to act early in the fermentation, giving bold sponges, but fall short in fermentation tolerance in cases where long fermentation periods are employed. Their application has so far been largely limited to the role of flour maturing agents, although efforts are being made to introduce them to bakers as dough maturing agents to be used in addition to ordinary dough conditioners. Their use has been prohibited in some foreign countries on the grounds that they are responsible for some types of bakers' dermatitis.

The approximate compositions of three widely used dough conditioners are reproduced above to serve as general examples of the types of salt mixtures that have been developed to meet the varying requirements presented by flours milled from different wheats, of different grades, or which have received varying degrees of bleach and aging. It should be understood by the baker that not all flours require the use of dough conditioners. Thus flours kept in long storage or which have received optimum

bleaching at the mill may frequently give better results with less than normal amounts of dough conditioners or without any at all.

Because of the marked effect upon dough characteristics produced by the oxidizing agents present in dough conditioners, these dough additives are generally used in very small increments on the order of 0.25 to 0.5 percent based on flour weight. The bulk of these products also usually consists of neutral ingredients, such as calcium salts and sodium chloride which have a slight tightening effect on the dough and ammonium salts which provide food for yeast. Starch or flour is generally used as filler to minimize the danger of over-treatment and to facilitate accurate weighing.

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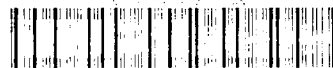(233) JOHNS, C. O., and JONES, D. B. *J. Biol. Chem. 28*, 77 (1916), cited by Geddes *(136)*.

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